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Photochemistry of 1,4-anthraquinone studied by steady-state and laser-flash photolysis

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Abstract

Photochemical reactions of 1,4-anthraquinone (1,4-AQ) whose lowest triplet state (T_1) is of the π, π^* type have been investigated in solution by means of steady-state and nanosecond laser flash photolyses. The absorption spectrum of triplet 1,4-AQ in the non-polar solvent is determined for the first time. The triplet state 1,4-AQ is quenched by the ground-state 1,4-AQ in CCl_4 to generate a dimerized product. In cycloalkanes, the final products obtained upon photoirradiation are adducts of the solvents to 1,4-AQ initiated with the 1,4-AQ ketyl radical. The formation of the 1,4-AQ ketyl radical originates from H-atom abstraction from cycloalkanes via the T_2 (n, π^*) state which is in thermodynamic equilibrium with the T_1 (π, π^*) state. In cycloalkenes and styrene, triplet 1,4-AQ gives the [2 + 2] cycloadducts forming the four-membered rings without H-atom abstraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 1,4-Anthraquinone; Laser flash photolysis; H-atom abstraction; [2 + 2] photocycloaddition; Quenching rate constant

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1. Introduction

Quinone compounds are known to play an important role in photobiological systems as well as in functional materials. A large number of photochemical and photophysical investigations have been carried out by means of product analysis and spectroscopic measurements [1–36]. In particular, *p*-benzoquinone, 1,4-naphthoquinone and 9,10-anthraquinone and their derivatives have been subjected to reveal the photochemical properties relating to their excited-state nature in solution. It is known that the molecules with the lowest triplet state (T_1) having an electronic character of n, π^* undergoes intermolecular H-atom abstraction and electron transfer. The photoproducts resulting from the photoreaction between paraquinones and hydrocarbons or olefins have been reported to be dihydroxy and oxetane derivatives, respectively, due to H-atom abstraction and $[2\pi + 2\pi]$ cycloaddition of the carbonyl group [7]. However, very little is known about the photochemical reactions of paraquinones with the T_1 state having a π, π^* character.

Recently, we have demonstrated anomalous photophysical properties of the excited-states of 1,4-anthraquinone (1,4-AQ) in solution [27–30]. These include the occurrence of the fluorescence from S_1 (n, π^*) and S_2 (π, π^*), both of which are in thermodynamic equilibrium with the T_1 (π, π^*) state. The excited-state ordering of 1,4-AQ is known to be S_2 (π, π^*) > S_1 (n, π^*) > T_2 (n, π^*) > T_1 (π, π^*). Molecules with the T_1 state of the π, π^* type are in general inert with respect to H-atom abstraction. Thus, the photochemical products and properties of triplet 1,4-AQ are of our great interest.

In the present study, we have analyzed the photoproducts of 1,4-AQ in CCl_4, cycloalkanes and cycloalkenes, and investigated the initial reactions of photoexcited 1,4-AQ toward the products. It is observed that triplet 1,4-AQ is quenched by the ground-state 1,4-AQ to produce the dimerized photoproduct. The final products obtained upon photo-irradiation in cycloalkanes are their adducts to 1,4-AQ. The initial reaction for these adducts is shown to be H-atom abstraction from cycloalkanes via the T_2 (n, π^*) state which is populated thermally from T_1 (π, π^*). Triplet 1,4-AQ is deactivated by olefins through the CT interaction to give the [2 + 2] cycloadducts having the four-membered rings. Photochemical properties of triplet 1,4-AQ in CCl_4 are discussed on the basis of the kinetic data.

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2. Experimental

1,4-Anthraquinone (1,4-AQ, Lancaster) was purified by passing through a silica-gel column using benzene as an eluent. Carbon tetrachloride (Merck, spectroscopic grade) was used as the solvent without further purification. 2-Methyltetrahydrofuran for a glass matrix at 77 K was purified by fractional distillation and stored over Na–K alloy in vacuo to remove traces of water. Cyclohexane (Aldrich, spectrophotometric grade), cyclopentane (Tokyo KASEI, GR-grade), cyclohexene (Kanto Chemical, Cica-reagent), cyclopentene (Tokyo KASEI, GR-grade) and styrene (Kanto Chemical, Cica-reagent) were used as supplied. Phenol was purified by the sublimation in vacuo. All the samples in quartz cells with a 10 mm path length prepared in the dark were degassed by several freeze-pump-thaw cycles on a high vacuum line. Steady-state and laser flash photolyses were carried out at 295 K.

Absorption spectra were measured by a U-best 50 spectrophotometer from JASCO. An extra-high pressure mercury lamp (USHIO, 250 W) with a cut-off filter ($\lambda > 390$ nm) was used as a light source for steady-state photolysis. Third harmonics (355 nm) of a nanosecond Nd^{3+}:YAG laser (JK Lasers HY-500) and a XeCl excimer laser (Lambda Physik, Lextra 50) at 308 nm were used for laser flash photolysis. The transient absorption spectra were taken with a USP-554 system from Unisoku which could take a transient absorption spectrum with one-shot laser pulse. The details of the detection system for the time profiles of the transient absorption have been described elsewhere [37]. The transient data obtained by laser photolysis were analyzed by using the least-squares best-fitting method.

To determine the quantum yields for the photodecomposition of 1,4-AQ, we have used monochromatic light at 405 nm from an extra-high-pressure mercury lamp passed through a monochromator. The number of incident photons at 405 nm was obtained by using the quantum yield for decomposition of 1,4-AQ in cyclohexane (0.095) which was determined in advance by using a low-pressure mercury lamp (254 nm) with a band-pass filter ($\lambda_{max} = 255$ nm) as a monochromatic light source. The photon flux at 254 nm was determined by using *N*-methyldiphenylamine in aerated methylcyclohexane as a chemical actinometer. The quantum yield for the formation of *N*-methylcarbazole from *N*-methyldiphenylamine has been established as 0.42 [38]. The procedure to determine the quantum yields was employed in the same way as that described in [39]. The photoproducts obtained by steady-state photolysis were isolated by silica-gel column chromatography with benzene as a developing solvent. The isolated products, purified by repeated recrystallizations from methylcyclohexane, were identified by the NMR spectroscopy.

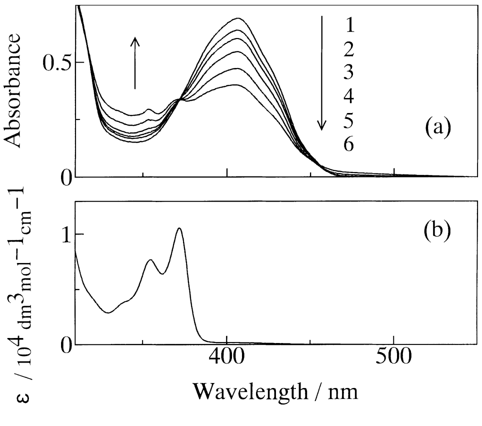
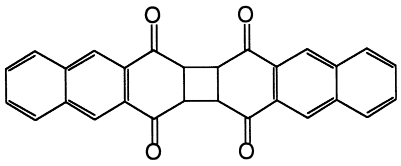


Fig. 1. (a) Absorption spectral change of 1,4-AQ in CCl_4 upon light irradiation ($\lambda > 390$ nm) for (1) 0; (2) 2; (3) 4; (4) 8; (5) 16 and (6) 30 min. (b) The absorption spectrum of product **1** in cyclohexane.

3. Results and discussion

3.1. Steady-state photolysis

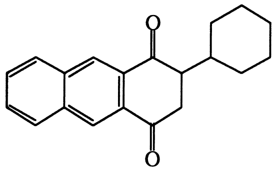
Fig. 1a shows the absorption spectral change of 1,4-AQ in degassed CCl_4 upon irradiation of $\lambda > 390$ nm light. The intensity of the absorption band of 1,4-AQ at 407 nm decreases with an increase of irradiation time, showing an isosbestic point at 373 nm. The quantum yield (Φ_d) of the decomposition was 0.008 ± 0.001. The photoproduct was identified as a dimerized compound of 1,4-AQ, **1**.



1

The absorption spectrum of **1** is shown in Fig. 1b. The UV and NMR data on **1** are given in Table 1. In the aerated solution of CCl_4, the photodecomposition was delayed.

In cyclohexane, during the spectral change of 1,4-AQ upon UV irradiation, an isosbestic point appeared at 363 nm as shown in Fig. 2a. The final absorption spectrum in Fig. 2a showed no appreciable change by aeration. The product that gave the final absorption spectrum was found to be a 1,4-AQ-cyclohexyl adduct, **2**. In cyclopentane, the final product was a cyclopentyl adduct of 1,4-AQ, **3**.



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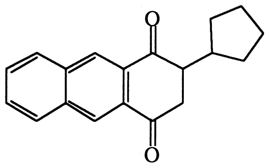


3

The photoproducts of 1,4-AQ with cycloalkanes are cycloalkyl adducts at the 2-position of 1,4-AQ skeleton.

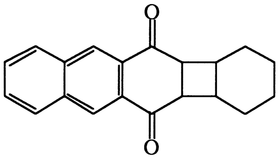
Change of solvent from cycloalkanes to cycloalkenes gave the photoproducts of another-type. In cyclohexene and

Table 1
The quantum yields of decomposition (Φ_d), the molar absorption coefficients (ε) at the peaks, and the NMR data of the photoproducts obtained

Product	Φ_d[a]	ε ($dm^3\,mol^{-1}\,cm^{-1}$)[b] (λ_{max} (nm))	δ (intensity, multiplicity, J in hertz)
1	0.008	10600 (370), 7700 (355)	4.08 (4H, s), 7.71 (4H, AA′BB′), 8.06 (4H, AA′BB′), 8.56 (4H, s)
2	0.095	3700 (357), 2100 (342)	0.96–1.84 (11H, m), 2.86 (1H, q, 7.5), 3.10 (1H, dd, 6.6, 3.3), 7.64 (2H, AA′BB′), 8.02 (2H, AA′BB′), 8.54 (2H, s)
3	0.073	3800 (357), 2150 (341)	1.23–1.84 (9H, m), 2.94 (H, dt, 8.8, 5.5), 3.08 (1H, dd, 16.3, 5.5), 3.24 (1H, dd, 16.3, 5.5), 7.68 (2H, AA′BB′), 8.06 (2H, AA′BB′), 8.58 (2H, s)
4	0.048	3700 (362), 2200 (345)	1.40 (2H, m), 1.65 (4H, m), 1.88 (2H, m), 2.75 (2H, br), 3.44 (2H, m), 7.68 (2H, AA′BB′), 8.09 (2H, AA′BB′), 8.70 (2H, s)
5	0.018	3600 (360), 2400 (344)	1.65 (2H, m), 1.97 (4H, m), 2.94 (2H, m), 3.16 (2H, d, 3), 7.70 (2H, AA′BB′), 8.08 (2H, AA′BB′), 8.70 (2H, s)
6	0.020	3250 (365), 2250 (350)	2.78–2.96 (2H, m), 3.60–3.65 (1H, m), 3.88–3.94 (2H, m), 7.35 (5H, m), 7.72 (2H, AA′BB′), 8.11 (2H, AA′BB′), 8.74 (1H, s), 8.77 (1H, s)

[a] Errors ±0.001.
[b] In cyclohexane.

cyclopentene, products **4** and **5** were obtained, respectively, both of which had cyclobutane rings at the 2- and 3-positions of 1,4-AQ.



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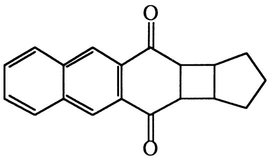

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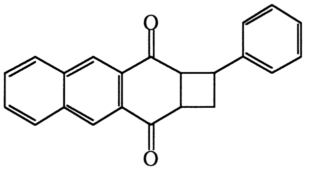
When styrene was used as the solvent, compound **6** was isolated.



6

Upon photolysis of 1,4-AQ in olefins, isosbestic points appeared during the absorption spectral change. The absorption spectra after photolysis in olefins were consistent with those of the isolated products. Thus, the formation of the four-membered ring compounds is characteristic of the photoexcited 1,4-AQ in olefins. Since the decomposition of 1,4-AQ was delayed in all the olefins used as well as in cycloalkanes, the reactive state of 1,4-AQ that contributes to all the pertinent product formation is considered to be triplet in nature. The quantum yields (Φ_d), UV and NMR data for the obtained photoproducts are summarized in Table 1.

3.2. Laser flash photolysis

3.2.1. Absorption spectrum and self-quenching of triplet 1,4-AQ

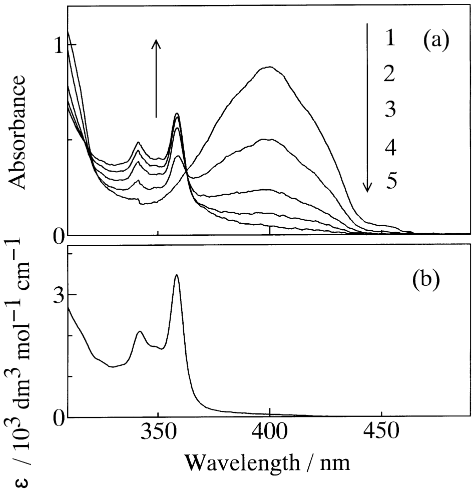


Fig. 2. (a) Absorption spectral change of 1,4-AQ in cyclohexane upon photoirradiation ($\lambda > 390$ nm) for (1) 0; (2) 10; (3) 20; (4) 40 and (5) 120 s. (b) The absorption spectrum of product **2** in cyclohexane.

Fig. 3 shows the transient absorption spectrum observed at 100 ns after 308 nm laser pulsing in the degassed CCl_4 solution of 1,4-AQ (1.0×10^{-4} mol dm^{-3}) at 295 K, together with the temporal absorbance change at 440 nm. The intensity of the observed absorption band decayed with the first-order rate of 1.7×10^5 s^{-1}, giving no residual

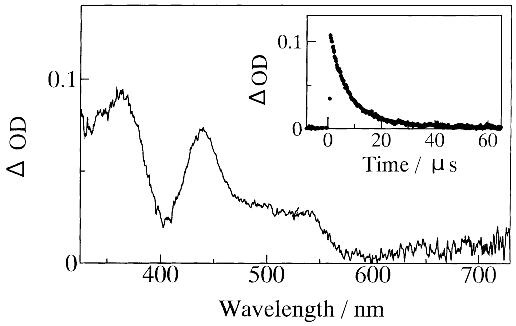


Fig. 3. Transient absorption spectrum observed at 100 ns after 308 nm laser photolysis in the 1,4-AQ (1.0×10^{-4} mol dm^{-3}) solution of CCl_4 at 295 K. The temporal absorbance change at 440 nm.

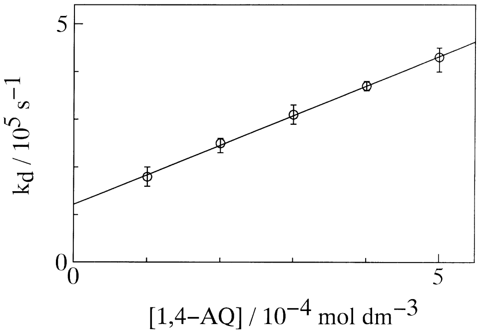


Fig. 4. Plots of the decay rates (k_d) of triplet 1,4-AQ against [1,4-AQ].

absorbance in the wavelength range 330–720 nm. In the presence of the dissolved oxygen, the decay was accelerated. Exactly the same absorption spectrum was observed in a glass matrix of 2-methyltetrahydrofuran at 77 K. Thus, the absorption spectrum in Fig. 3 can be safely attributed to that of triplet 1,4-AQ.

The decay rate (k_d) of triplet 1,4-AQ was found to depend on the concentration of 1,4-AQ, [1,4-AQ]. Fig. 4 shows the k_d values plotted as a function of [1,4-AQ]. The plots give a straight line, indicating that k_d is expressed by Eq. (1)

$$k_d = k_0^{SQ} + k_{SQ}[1,4\text{-AQ}] \qquad (1)$$

where k_0^{SQ} and k_{SQ}, respectively, represent the decay rate of triplet 1,4-AQ at the infinitely diluted concentration of 1,4-AQ, and the rate constant for the self-quenching. From the intercept and slope of the straight line, the values of k_0^{SQ} and k_{SQ} are determined to be $1.2 \times 10^5\,s^{-1}$ and $6.4 \times 10^8\,dm^3\,mol^{-1}\,s^{-1}$, respectively. The self-quenching rate constant is smaller than that of the diffusion limit of CCl_4 ($6.7 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$ at 20°C [40]). The reciprocal of the k_0^{SQ} value (8.3 ms) corresponds to the lifetime of triplet 1,4-AQ in CCl_4 at 22°C free of the interaction with the ground-state 1,4-AQ. This value agrees in the magnitude of order with the lifetime (30 ± 10 ms at 15°C [30]) of the fluorescence from S_1 (n, π^*) which is in a thermal equilibrium with T_1 (π, π^*).

3.2.2. Quenching of triplet 1,4-AQ by cycloalkanes and olefins

The quenching experiments on triplet 1,4-AQ by cycloalkanes and olefins in degassed CCl_4 were carried out by monitoring the decay profile of triplet 1,4-AQ at 440 nm. The decay of triplet 1,4-AQ with the first-order rate (k_{obsd}) was accelerated proportionally to the concentration of all the quenchers used. The quenching rate constants (k_q) of triplet 1,4-AQ by quenchers [Q] were obtained from the slope of the plots of k_q versus [Q].

$$k_{obsd} = k_d + k_q[Q] \qquad (2)$$

The values of k_q thus obtained are listed in Table 2. All the values of k_q are smaller than that of diffusion-control rate of CCl_4.

Table 2
The quenching rate constants and efficiencies of the AQK formation

Quencher	k_q ($dm^3\,mol^{-1}\,s^{-1}$)[a]	α_{rad}[a]
Cyclohexane	2.4×10^6	0.57
Cyclopentane	1.6×10^6	0.55
Cyclopentene	2.9×10^8	~0
Cyclohexene	2.1×10^8	~0
Styrene	8.8×10^8	~0
TMB[b]	5.0×10^9	~0

[a] Errors ±5%.
[b] 1,2,4,5-Teteramethoxybenzene.

In the presence of cyclohexane, an increase of the optical density was observed at 480 nm with the first-order rate identical with that of the decay of 1,4-AQ ($4.6 \times 10^6\,s^{-1}$). Fig. 5 shows the transient absorption spectrum obtained after the depletion of triplet 1,4-AQ in the presence of cyclohexane. The similar transient absorption was obtained after the depletion of triplet 1,4-AQ in the presence of cyclopentane and phenol. It is known that phenol behaves as an H-atom donor against triplet carbonyl compounds to give their ketyl radicals [31–36,41,42]. Thus, we ascribe the obtained transient spectrum to that of 1,4-AQ ketyl radical (AQK). The production of AQK originates from H-atom abstraction of triplet 1,4-AQ from cycloalkanes and phenol. The decay profile of AQK was unable to be fitted by the first- or second-order kinetic analysis.

The quantum yield (Φ_{AQK}) of the AQK formation was determined by Eq. (3)

$$\Phi_{AQK} = \Delta OD_{480}\,\varepsilon_{480}^{-1} I_{abs}^{-1} \qquad (3)$$

where ΔOD_{480}, ε_{480} and I_{abs}, respectively, are the optical density due to the formation of AQK at 480 nm (see Fig. 5), the molar absorption coefficient ($6700\,dm^3\,mol^{-1}\,cm^{-1}$ [36]) of AQK at 480 nm, and the quanta of the incident laser pulse absorbed by 1,4-AQ at 355 nm. The quantity of I_{abs} was determined by using the absorption of triplet benzophenone at 520 nm as an actinometer [43]. The Φ_{AQK} value is found to increase with an increase of the quencher concentration. The Φ_{AQK} value is relating also to the kinetic

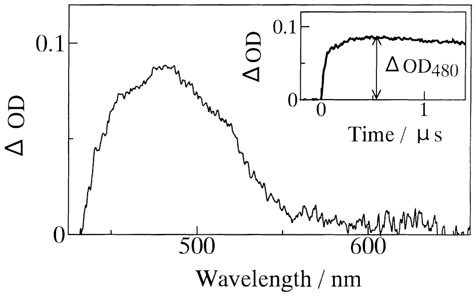


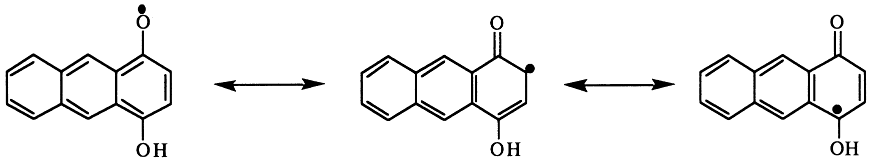
Fig. 5. The transient absorption spectrum obtained at 600 ns after 308 nm laser pulsing in the 1,4-AQ ($1.0 \times 10^{-4}\,mol\,dm^{-3}$) cyclohexane ($1.9\,mol\,dm^{-3}$) system in CCl_4. The time profile of the absorbance change at 480 nm.

parameters, k_d and k_q in Eq. (4)

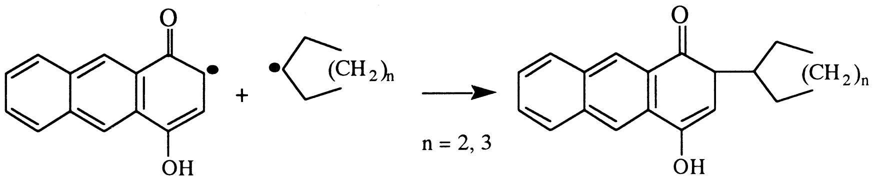
$$\Phi_{\mathrm{AQK}} = k_q[\mathrm{Q}]\alpha_{\mathrm{rad}}\Phi_{\mathrm{ISC}}(k_d + k_q[\mathrm{Q}])^{-1} \tag{4}$$

where α_{rad} and Φ_{ISC} are, respectively, the efficiency of the AQK formation in the triplet state of 1,4-AQ and the triplet yield of 1,4-AQ. The Φ_{ISC} value is regarded to be unity, since the quantum yield of emission from photoexcited 1,4-AQ in CCl_4 has been reported to be negligibly small ($<10^{-4}$ [30]). By best-fitting of Eq. (4) to the experimental values of Φ_{AQK} with the use of $k_d = 1.8 \times 10^5\,\mathrm{s}^{-1}$ and $k_q = 2.4 \times 10^6\,\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$, the α_{rad} value for cyclohexane was obtained to be 0.57 ± 0.02. The values of α_{rad} for cyclopentane and phenol were 0.55 and 0.23, respectively. The residual efficiency ($1 - \alpha_{\mathrm{rad}}$) is considered to originate from the induced-quenching process which is inherent to the intermolecular H-atom abstraction [44]. The mechanism of induced-quenching concomitant with H-atom abstraction has been interpreted in terms of the intersystem crossing induced by charge-transfer interaction [45].

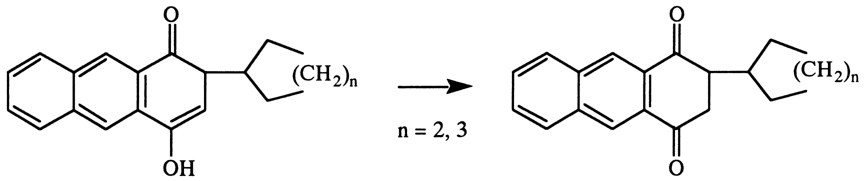
Upon the photolysis of 1,4-AQ in the presence of cycloalkanes, products **2** and **3** are obtained as the final product whereas the initial product is found to be the AQK radical. The formation process of products, **2** and **3** from the AQK radical can be rationalized as follows. The AQK radical can have resonance structures as illustrated below.



When AQK encounters the H-atom abstracted radicals of cycloalkanes, a new chemical bond at the 2-position of the 1,4-AQ skeleton is expected to be formed.



After the formation of the C–C-bond at the 2-position, the keto-enol isomerization may cause to produce the final products.



The quantum yields for **2** and **3** formation were obtained to be less than 0.1, which is relatively small as compared with the α_{rad} values for cycloalkanes (0.56). This large value of α_{rad} can be interpreted by considering the spin multiplicity. When H-atom abstraction occurs in triplet 1,4-AQ with cycloalkanes, a triplet radical pair of AQK and cycloalkyl radicals is expected to be formed in solvent cages according to the spin-conservation rule. The geminate recombination between AQK and cycloalkyl radicals in solvent cages is forbidden due to triplet multiplicity. Intersystem crossing of the triplet radical pair for recombination requires a relatively longer time than for radical escaping from the solvent cage. Thus, without intersystem crossing, AQK and cycloalkyl radicals will readily become free radicals in a diffusion process.

The excited-state ordering of 1,4-AQ is known to be S_1 (n, π^*) > T_2 (n, π^*) > T_1 (π, π^*), where S_1 and T_1 can be in a thermodynamic equilibrium at room temperature due to the energy difference as small as $6.0\,\mathrm{kcal\,mol}^{-1}$ [27,30]. Thus, the T_2 state must be populated thermally from T_1 at 295 K. The electronic character of the T_1 state of 1,4-AQ has been revealed to be π, π^* which is inert for H-atom abstraction whereas that of T_2 (n, π^*) is reactive. Formation of AQK indicates that triplet 1,4-AQ abstracts H-atom via the T_2 state populated thermally from T_1. The transient absorption spectrum of triplet 1,4-AQ (Fig. 3) is considered to consist of the mixture of absorption for the $T_m \leftarrow T_1$ and $T_n \leftarrow T_2$ transitions, where m may be or may not be different from n. The shape of the absorption spectrum of triplet 1,4-AQ obtained in CCl_4 is quite different from that in acetonitrile [36]. This may be due to the effect of the solvent polarity to the energy levels of T_1 (π, π^*) and T_2 (n, π^*), resulting in the change in the absorption spectrum of triplet 1,4-AQ.

When triplet 1,4-AQ is quenched by olefins, no transient absorption was detected in the wavelength region 400–800 nm after the depletion of triplet 1,4-AQ. In the photochemical reactions of 1,4-AQ with olefins, however, cycloaddition forming the four-membered ring compounds, **4**, **5** and **6** was observed. Unfortunately, neither the initial intermediates leading to the products having the cyclobutane ring nor formation of the final products, **4**, **5** and **6** was detected in the transient absorption measurement. If we assume a concerted mechanism for the cyclobutane-ring formation, the quenching rate constants (k_q) obtained in the present work can be regarded as the rate constants of the formation of the final products. Furthermore, H-atom abstraction of 1,4-AQ from olefins was not observed. This can be rationalized by considering that the rate constant of H-atom abstraction via T_2 (n, π^*) is smaller ($\sim 10^6$ dm^3 mol^{-1} s^{-1}) than that for the cyclobutane-ring formation ($\sim 10^8$ dm^3 mol^{-1} s^{-1}). We expect that the carbonyl compounds having the large energy separation between T_1 (π, π^*) and T_2 (n, π^*) would not undergo H-atom abstraction from any H-atom donors. Noteworthy is that no production of oxetane-type adducts with olefins was found for 1,4-AQ. This may be characteristic to the carbonyl compounds with the T_1 state of π, π^* type because of the relatively low spin-density on the carbonyl groups in the π, π^* state. Further studies of photochemical properties of the C=O containing compounds with the T_1 state of π, π^* type are now in progress.

4. Conclusion

Photochemical reactions of 1,4-AQ whose lowest triplet state is of the π, π^* type have been investigated in CCl_4 by means of steady-state and nanosecond laser flash photolyses. The absorption spectrum of triplet 1,4-AQ is determined for the first time (Fig. 3). Triplet 1,4-AQ is quenched by the ground-state 1,4-AQ with the rate constant of 6.4×10^8 dm^3 mol^{-1} s^{-1} to generate the dimerized product, **1** with the quantum yield of 0.008. The lifetime of triplet 1,4-AQ in CCl_4 free of self-quenching is obtained to be 8.3 ms. In cyclohexane and cyclopentane, the final products obtained upon photoirradiation are adducts of the solvents to 1,4-AQ, **2** and **3**. In the presence of cycloalkanes, the 1,4-AQ ketyl radical is produced with the quantum yield of 0.56 and with the rate constant of $\sim 10^6$ dm^3 mol^{-1} s^{-1}. The initial reaction of 1,4-AQ with cycloalkanes is revealed to be H-atom abstraction from cycloalkanes via the T_2 (n, π^*) state which is in a thermodynamic equilibrium with T_1 (π, π^*). In cyclohexene, cyclopentene and styrene, triplet 1,4-AQ gives the [2 + 2] cycloadducts forming the four-membered rings, **4**, **5** and **6**. The quenching rate constants of triplet 1,4-AQ by the olefins are determined to be about 10^8 dm^3 mol^{-1} s^{-1}.

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