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Spectroscopic Studies on the Intramolecular Hydrogen Abstraction Reactions of *n*-Alkyl Anthraquinone-2-carboxylates

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Chain length dependence of the intramolecular hydrogen abstraction reaction of *n*-alkyl anthraquinone-2-carboxylates (AQ-*n*, n=2—20) has been studied by steady-state photolysis, phosphorescence, laser flash photolysis, and two-step laser induced fluorescence spectroscopies. All the results indicate that the excited triplet of the anthraquinone chromophore abstracts a hydrogen atom from its methylene side chain, whose rate increases with increasing chain length. The rate constant of AQ-8 is 1×10^4 s^{-1} and the increase in the rate is about 1.5×10^4 s^{-1} per one additional methylene unit for $n \geqslant 10$.

For many years chemistry and physics of bifunctional chain molecules have drawn much attention of polymer chemists, ESR and NMR spectroscopists, photochemists, photophysicists, and synthetic organic chemists, as reviewed in the literature.[1] It is because we can elucidate structural and energetic factors required in a reaction. Concerning with photochemistry, remote hydrogen abstraction of *n*-alkyl benzophenone-4-carboxylates, for example, have been extensively studied by Winnik and coworkers, to show how chain motion affects their photochemistry and photophysics.[2] In intramolecular excimer fluorescence of pyrene–$(CH_2)_n$–pyrene (n=2—22), fluorescence yields of the excimer were reported to be maximum at n=3 and minimum at n=7.[3] Switching of photochemical reaction pathways was found for redox reaction of a series of *N*-[*ω*-(*p*-nitrophenoxy)-alkyl]anilines.[4]

We have studied the magnetic field effects on the intermolecular hydrogen abstraction reaction of anthraquinones in aqueous sodium dodecyl sulfate (SDS) micellar solution, where a SDS surfactant acts itself as a hydrogen donor.[5] As intramolecular analogue of the reaction between excited triplet anthraquinone and SDS in a micelle, we designed a intramolecular reaction of anthraquinone with its methylene side chain. The excited triplet state is highly reactive compared with that of benzophenone so that the reaction processes may be followed precisely by time-resolved spectroscopic technique. This paper describes the effect of methylene chain lengths on photochemical and photophysical processes of *n*-alkyl anthraquinone-2-carboxylates, studied by steady-state photolysis, phosphorescence, laser flash photolysis, and two-step laser excitation fluorescence spectroscopies.[6]

Experimental

Chemicals. *n*-Alkyl anthraquinone-2-carboxylates (AQ-*n*, n=2—20) were synthesized by the condensation of anthraquinone-2-carboxylic acid sodium salt and *n*-alkyl bromides and purified by column chromatography and recrystallization. Typical analytical data of AQ-14 are as follows: mp 102 °C. IR(KBr) 2950—2840 (methylene), 1725 (aromatic ester), 1670 cm^{-1} (aromatic ketone). ^{1}H NMR (60 MHz, $CDCl_3$) δ=0.8—0.96 (t, 3H, CH_3–), 1.25 (s, 24H, –CH_2–), 4.23—4.45 (t, 2H, –CO–O–CH_2–), 7.63—8.80 (m, 7H, aromatic). Found: C, 77.64; H, 8.22%. Calcd for $C_{29}H_{36}O_4$: C, 77.64; H, 8.09%. Mass spectra; m/z 448 (M^+). Melting points of AQ-*n* are listed in Table 1.

EP Grade 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) was purified by a column of basic aluminum oxide (1 m) and 3-methylpentane was distilled from $LiAlH_4$. Freon 113 was used in order to avoid intermolecular hydrogen abstraction reaction of AQ-*n* from solvent. Sample solutions were deaerated by several freeze-pump-thaw cycles, when necessary.

Apparatus. In steady-state photolysis, a 3 ml aliquote of the sample solution was irradiated with a 500 W xenon arc lamp filtered with a combination of a color glass (Toshiba UV-D33S) and a $NiSO_4$–$CoSO_4$ aqueous solution ($\lambda_{max}\approx330$ nm). The UV absorption spectral changes were recorded by a Hitachi U-3200 spectrophotometer.

Phosphorescence spectra were measured with a Hitachi MPF-4 spectrophotometer. The lifetimes were determined with an Ortec single photon counting system equipped with a PRA light pulser.

Transient absorption spectra were obtained by using an XeCl excimer laser (Lambda Physik EMG-50E, 308 nm) and a xenon arc lamp as an exciting and a probe light source, respectively. Transient signal on an Iwatsu TS-8123 storagescope was fed into a Fujitsu FM-11BS microcomputer for analysis.

Two-step laser induced fluorescence (TS-LIF) was measured by using an excimer laser (308 nm) and a N_2 laser-pumped dye laser (Molectron UV-12 and DL-14, 430 nm) as the first and the second laser. A homemade variable delay circuit was used for the timing of two lasers.

Table 1. Melting Points of *n*-Alkyl Anthraquinone-2-carboxylates (AQ-*n*)

n	Melting point/°C	n	Melting point/°C
2	149—150	12	97—98
3	101—102	14	102
4	122—123	16	104—105
6	83	18	107
8	86—87	20	107—108
10	93—94		

Results

Steady-State Photolysis. Figure 1 shows a typical UV absorption spectral change of AQ-14 in Freon 113 solution upon photoirradiation, indicating photoreaction of this molecule. After photolysis, the solution becomes fluorescent as shown in the figure. Photoproducts, whose absorption and fluorescence bands appear around 350—500 and 450—600 nm, respectively, may be attributable to the cyclization products, since cyclic photoproducts in the photoinduced intramolecular hydrogen abstraction of n-alkyl benzophenone-4-carboxylates2) and a fluorescent photoadduct of anthrasemiquinone to a SDS surfactant in the photoreaction of anthraquinone5,7) were reported (see bellow).

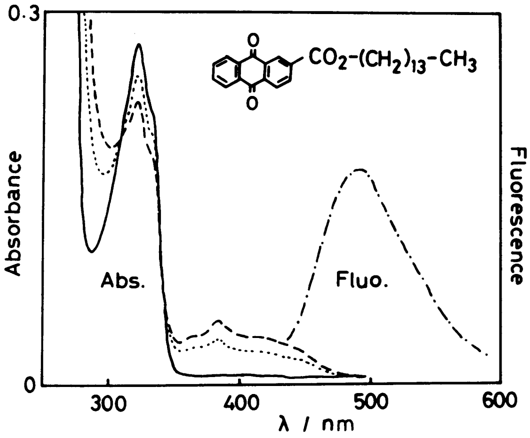


Fig. 1. Absorption and fluorescence spectra of AQ-14 in Freon 113 during photolysis. ——, before irradiation; -----, after 2 min irradiation, --- and —·—, after 4 min irradiation.

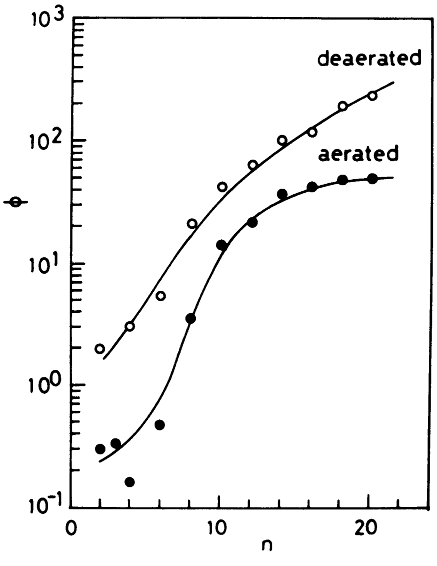


Fig. 2. Relative yields ϕ of disappearance of AQ-n in Freon 113.

Relative yield ϕ of disappearance of AQ-n were determined from the initial absorption intensity changes around 320 nm by the procedure described in a previous paper.5) As shown in Fig. 2, ϕ is very small at shorter methylene chain length ($n<6$) and shows a sudden increase around $n=8$. Photolysis was also carried out in aerated Freon 113 solution of AQ-n (Fig. 2). The yields in aerated solutions are always smaller than those in deaerated solutions. The fact indicates that dissolved oxygen is also involved in the reaction though its mechanism is unknown at the present stage.

Phosphorescence. In order to clarify the primary step of the present photoreaction, we first examined the excited triplet of AQ-n by phosphorescence. Figure 3 shows phosphorescence spectra of AQ-n observed at room temperature and of AQ-2 at 77 K. In the spectra at room temperature, the band maxima appear at 435, 464, 502, 548, and 602 nm, and the shortest wavelength band at 435 nm disappears in the

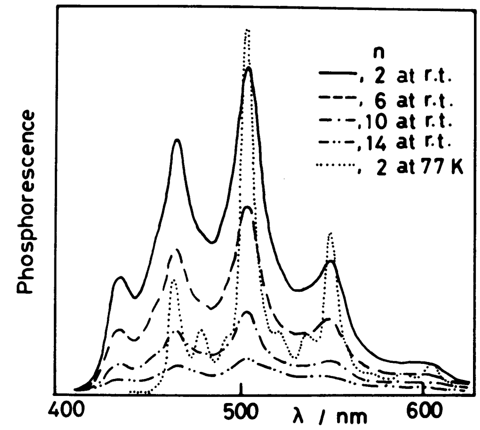


Fig. 3. Phosphorescence spectra of AQ-n at room temperature and 77 K.

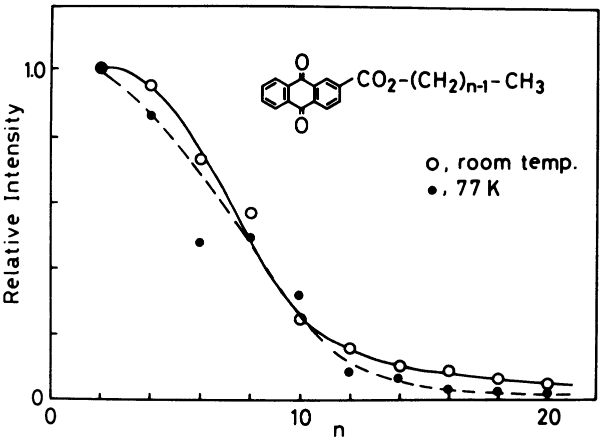


Fig. 4. Relative phosphorescence intensities of AQ-n at room temperature and 77 K. The intensities were normalized for that of AQ-2 at the respective temperature.

Table 2. Lifetimes (μs) of Excited Triplet State of AQ-*n*, Determined by Phosphorescence $\tau_{\mathrm{P}}(n)$ and Laser Flash Photolysis $\tau_{\mathrm{LF}}(n)$[a]

n	τ_{P}	τ_{LF}	*n*	τ_{P}	τ_{LF}
2	75.8	48.7	12	11.9	10.0
4	70.4	42.9	14	7.9	7.3
6	52.3	38.1	16	6.8	6.0
8	40.7	30.4	18	5.5	5.2
10	19.0	12.6	20	4.3	4.5

Experimental errors are ±10 and ±20% for τ_{P} and τ_{LF}, respectively.

spectrum at 77 K. The energy difference between two successive bands are 1437, 1631, 1672, and 1637 cm^{-1}. Since the band progression from the second band is characteristic of the C=O stretching vibration, the 0–0 band of the phosphorescence is assigned to the one at 464 nm, and the lowest triplet state is of n,π* nature. The assignment is compatible with the n,π* nature of the lowest triplet state of anthraquinone.[8–11] The shortest wavelength band at 435 nm, which disappears at 77 K, may be attributable to the emission from the thermally-populated higher triplet state. It is uncertain at the present stage whether it is the second triplet state or the vibronic state of the lowest one.[12]

The relative phosphorescence intensities and lifetimes of AQ-*n* depend on the chain length *n* at room temperature as shown in Fig. 4 and Table 2, respectively. The lifetimes of AQ-*n* may be free from triplet–triplet (T–T) annihilation reaction, since they were obtained under low excitation density. Both phosphorescence intensities and lifetimes decrease with increasing the methylene chain length, *n*, suggesting that intramolecular reaction, i.e., hydrogen abstraction, is responsible for the lifetime of the excited triplet states. Furthermore, as shown in Fig. 4, the phosphorescence intensity dependence on the chain length observed at 77 K resembles that observed at room temperature. The facts may imply that the conformational distribution of the chain at room temperature is frozen at 77 K. Thus the phosphorescence lifetimes of AQ-*n* at 77 K may be determined by the intramolecular hydrogen abstraction. However, it is of interest that photoirradiation of AQ-14 in 3-methylpentane rigid matrix at 77 K did not show any appreciable change in its UV absorption spectrum. Probably, back reaction is fast in the rigid matrix because of conformational rigidity of the methylene chain in it.

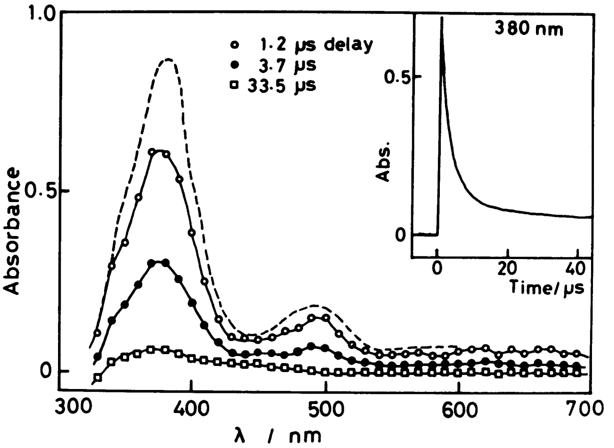


Fig. 5. Transient absorption spectra of AQ-14 in Freon 113. A broken line is the spectrum of AQ-2 at a 0.5 μs delay after laser excitation. Inset: A typical decay profile of transient absorption of AQ-14 monitored at 380 nm.

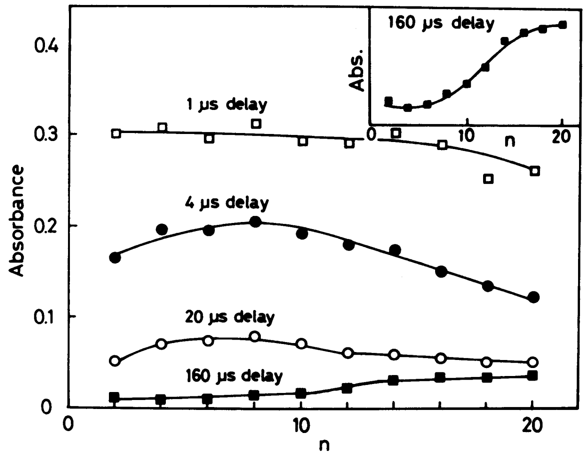


Fig. 6. Plots of transient absorption intensities at several delaytimes after laser excitation for AQ-*n*. Inset: Manification of the intensities at a 160 μs delay.

Transient Absorption Spectra. Figure 5 shows transient absorption spectra of AQ-14 in Freon 113. As shown in the inset, decay of a transient absorption at 380 nm reaches a constant value around a 50 μs delay after laser excitation. In the transient absorption spectra at the present time scale (ca. 50 μs), there may be at least three species, i.e., excited triplet anthraquinone, semiquinone, and photoproducts. The absorption bands peaked around 380 and 500 nm, observed at a 1.2 μs delay, is mostly attributable to the T–T absorption of the anthraquinone chromophore. It is because similar spectra were observed for AQ-2, as shown in Fig. 5, and other molecules with *n*=3—20 in the μs time region, and the lifetime is comparable with its phosphorescence lifetime. On the other hand, the bands peaked around 380 and 450 nm, observed at a 33.5 μs delay, may be assigned to cyclization photoproducts, since they are similar to those of photoproducts observed in the steady-state photolysis (Fig. 1). The spectrum in the middle stage of the delay time might be attributable to the semiquinone radical, though its rigorous assignment is impossible. The decay of the semiquinone radical seems to be fast as observed in the reaction of the anthrasemiquinone radical in

Table 3. Relative TS-LIF Intensities $I(n)$ and Risetimes $\tau_R(n)$ of AQ-n[a]

n	$I(n)$	$\tau_R(n)$
		μs
10	0.2	17.5
12	0.6	14.9
14	1.0	10.6
16	1.6	7.7
18	1.1	4.8
20	1.9	4.7

a) $I(n)$ are the intensities at a 70 μs delay after the first laser excitation. Experimental error is ±10—20%.

micellar solutions.[5]

In Fig. 6, transient absorption intensities at several delaytimes are shown as a function of n. The absorption intensities at a 4 μs delay decrease with increasing n, though those immediately after the laser excitation (1 μs delay) are almost independent of n. The n dependence of the absorption intensities at 4 and 20 μs delays is reflection of the lifetime shortening of the triplet states with increasing n. In contrast, the intensities at about 160 μs delay, which may be attributable to the photoproducts, gradually increases with increasing n, indicating the increase in the reaction yield with n.

The triplet lifetimes, estimated from the decay of the transient absorption at 380 nm, are listed in Table 2. The lifetimes estimated from the transient absorption are in good agreement with the phosphorescence lifetimes for longer methylene chain molecules (n=12—20). For the shorter chain molecules (n=2—6), triplet lifetimes estimated from the transient absorption is shorter than the phosphorescence lifetimes. This is mostly ascribed to the T–T annihilation due to the high excitation density in laser flash photolysis. Dependence of the lifetimes on n is almost the same as that of phosphorescence lifetimes. These observations present spectroscopic evidence that not physical but chemical quenching by methylene chain in the excited triplet determines its lifetime for long-chain molecules.

Two-Step Laser Induced Fluorescence. It was further attempted to monitor the initial yield of photoproducts with the aid of two-step laser induced fluorescence (TS-LIF) technique, since the cyclization products strongly fluoresce. This technique was proved to be effective to monitor the dynamics of fluorescent intermediates and products.[5,13] Figure 7 shows time-resolved TS-LIF spectra of AQ-14. The fluorescence band around 500 nm may be assigned to the photoproducts, since its spectrum and lifetime (22 ns) agree with those of photoproducts obtained from the steady-state photolysis (Fig. 1). As shown in the inset of Fig. 7, the fluorescence from photoproducts increases in intensity by increasing the delaytime between the first and second lasers, and reaches a plateau around 50 μs or so.

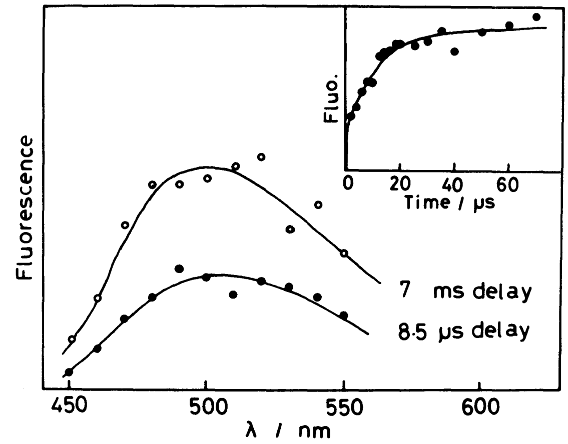
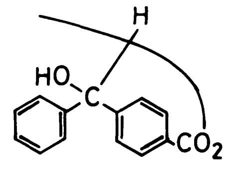


Fig. 7. Two-step laser induced fluorescence (TS-LIF) spectra of AQ-14 in Freon 113. Inset: Time profile of the TS-LIF intensity at 520 nm observed at several delaytimes.

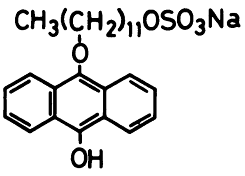
The relative yield and formation rate of the products were estimated from the relative TS-LIF intensities at a 70 μs delay and the growth curve of TS-LIF, respectively (Table 3). It is shown that the product yield determined by the TS-LIF increases with increasing n from 10 to 20, in accord with the increase in the formation rate (inverse of the risetime).

Discussion

A considerable effort has been made to elucidate photochemistry and photophysics of n-alkyl benzophenone-4-carboxylates (BP-n) by Winnik and coworkers.[2] According to their study, excited triplet benzophenone abstracts a hydrogen atom from its methylene side chain, leading to the cyclization products:



On the other hand, quite a few papers have been reported on the primary photochemical processes of quinones and benzophenones, in aqueous micellar solutions.[5,7,14—17] In micellar solution, their excited triplet states abstract a hydrogen atom from the methylene chain of a surfactant, resulting in the formation of an adduct of semiquinone (or ketyl radical) to the surfactant as a cage product. Upon photolysis of anthraquinone in micellar solution, the fluorescent products were obtained as the cage product:[7]



On analogy with the photoreactions mentioned above, photophysics and photochemistry of AQ-*n* may be described by the following scheme:

$$\text{AQ-}n \xrightarrow{h\nu} {}^1\text{AQ*-}n \tag{1}$$

$${}^1\text{AQ*-}n \longrightarrow {}^3\text{AQ*-}n \tag{2}$$

$${}^3\text{AQ*-}n \longrightarrow \text{AQ-}n + \text{phos.} \tag{3}$$

$${}^3\text{AQ*-}n \longrightarrow \text{AQ-}n \tag{4}$$

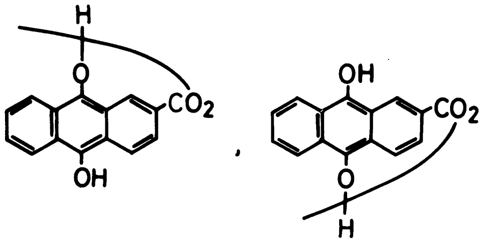
$${}^3\text{AQ*-}n \longrightarrow {}^3\text{BR} \tag{5}$$

$${}^3\text{BR} \rightleftarrows {}^1\text{BR} \tag{6}$$

$${}^1\text{BR} \longrightarrow \text{P-}n. \tag{7}$$

The excited triplet state ^{3}AQ*-*n* of the anthraquinone chromophore is generated by the photoexcitation ((1) and (2)). While it phosphoresces (3), it abstracts a hydrogen atom from its methylene side chain, leading to a triplet biradical ^{3}BR. Triplet–singlet intersystem crossing of the biradical (6) results in the formation of a cage product P-*n*. Bimolecular reactions in the excited triplet ^{3}AQ*-*n* as well as those in triplet biradical might occur. A triplet biradical might be quenched by impurities. These reactions are not included in the scheme, though they might take place. In aerated solution, quenching of the excited triplet ^{3}AQ*-*n* as well as the biradical by dissolved oxygen may be responsible for the deactivation of the respective species.

As already shown for the reaction of *n*-alkyl benzophenone-4-carboxylates (BP-*n*),[2] the position of the hydrogen atom, which is abstracted by triplet anthraquinone, may spread over the polymethylenes, whose reaction probability seems proportional to the frequency of the collision of two sites. Further, in the present molecules, either one of two carbonyls at 9- and 10-positions, which are not equivalent with respect to the carboxyl group at 2-position, may abstract the hydrogen atom. Thus analysis of the reaction products is highly complicated. For example, in a thin-layer chromatogram of a photolyzed solution of AQ-14, at least four fluorescent products were detected, which may be isomers of different ring size, though chemical identification failed because of difficulty in isolation. These products change into nonfluorescent products upon aeration. This change is very similar to that described in the photoadduct of anthrasemiquinone to the surfactant in a SDS micellar solution, which may be attributable to the keto–enol isomerization.[7] Therefore, the main photoproducts are mostly ascribed to the coupling products at the two radical centers, i.e., cyclization products P-*n*:



All the observations mentioned in the previous section can be now discussed how the methylene chain length affects the intramolecular reaction efficiency between the excited triplet anthraquinone and the methylene side chain. In steady-state photolysis, the relative yield of disappearance of AQ-*n* increases with increasing the methylene chain lengths (Fig. 2), suggesting that the hydrogen abstraction of the excited triplet anthraquinone chromophore from its methylene side chain is responsible for the net photoreaction. This conclusion is confirmed from the phosphorescence, transient absorption, and TS-LIF measurements. Dependence of the phosphorescence intensities and lifetimes on methylene chain length *n* (Figs. 3 and 4, and Table 2) indicates that the excited triplet is quenched by the collision with its methylene chain. It is further verified, by transient absorption (Fig. 6 and Table 2) and TS-LIF (Table 3), that the quenching is not physical but chemical one, which generates biradicals, followed by the formation of fluorescent products. Collision between the carbonyl carbon atom at the anthraquinone chromophore in the excited state and the hydrogen atom at the methylene chain is a rate controlling step, whose frequency depends on the length of the chain. In the short-chain molecules, e.g., AQ-2, the steric hindrance avoids its reaction. In the long-chain molecules ($n \geqslant 10$), the reaction rate increases in accord with the collision frequency between the carbonyl and the methylene groups.

Now let's estimate the rate of hydrogen abstraction reaction. The lifetime $\tau_\text{T}(n)$ of the excited triplet ^{3}AQ*-*n* is given by the following equation,

$$1/\tau_\text{T}(n) = k_3 + k_4 + k_5(n). \tag{8}$$

By assuming that lifetime $\tau_\text{T}(2)$ of AQ-2 is determined only by the physical processes (3) and (4), the rate constant $k_5(n)$ of intramolecular reaction of AQ-*n* can be estimated as follows;

$$k_5(n) = 1/\tau_\text{T}(n) - 1/\tau_\text{T}(2). \tag{9}$$

Experimentally, lifetimes of the triplet state were obtained as phosphorescence lifetimes $\tau_\text{P}(n)$ and lifetimes $\tau_\text{LF}(n)$ of T–T absorption. Thus we can

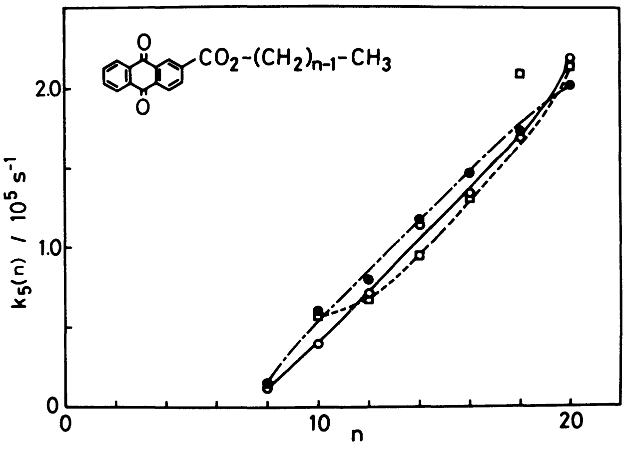


Fig. 8. Plots of the rate constant $k_5(n)$ of the intramolecular hydrogen abstraction against methylene chain length n. $k_5(n)$ were determined from phosphorescence lifetimes $\tau_P(n)$, ○, lifetimes $\tau_{LF}(n)$ of T–T absorption at 380 nm, ●, and risetimes $\tau_R(n)$ of photoproducts, □. See text.

determine $k_5(n)$ from the following equations:

$$k_5(n) = 1/\tau_P(n) - 1/\tau_P(2) \qquad (10)$$

and

$$k_5(n) = 1/\tau_{LF}(n) = 1/\tau_{LF}(2). \qquad (11)$$

The plots of Eqs. 10 and 11 against chain length n are given in Fig. 8. The $k_5(n)$ obtained by Eqs. 10 and 11 are in good agreement with each other as expected. In contrast with the phosphorescence lifetimes, triplet lifetimes of short-chain molecules ($n<8$) obtained from laser flash photolysis may be slightly shortened due to the T–T annihilation, which is not included in the above reaction scheme. For molecules with $n>8$, however, the triplet lifetimes are controlled predominantly by the rate $k_5(n)$ of intramolecular hydrogen abstraction.

In the TS-LIF measurements, the risetimes $\tau_R(n)$ of the fluorescence from the products may represent the formation rates. As discussed above, all the results indicate that the rate controlling step may be the reaction in the triplet state. If this is the case, the rate of product formation may be equal to the deactivation rate of the excited triplet,

$$1/\tau_R(n) = k_3 + k_4 + k_5(n). \qquad (12)$$

Since $k_5(n) > k_3 + k_4$ for long-chain molecules as shown from the analysis of the excited triplet lifetimes, the following equation may approximately hold for $n \geqslant 10$:

$$k_5(n) \sim 1/\tau_R(n). \qquad (13)$$

The plots of Eq. 13 against chain length n are also shown in Fig. 8. The k_5 values estimated from the risetimes of products (Eq. 13) coincide with those from lifetimes of the excited triplet states (Eqs. 10 and 11). The facts again demonstrate that the rate controlling step is the intramolecular hydrogen abstraction reaction in the excited state $^3AQ^*$-n for $n \geqslant 10$.

From the slope of the figure, we can conclude that the reaction rate of AQ-8 is 1×10^4 s^{-1} and the increase is 1.5×10^4 s^{-1} per one additional methylene unit for $n>8$.

Chain length dependence of intramolecular hydrogen abstraction of n-alkyl benzophenone-4-carboxylates (BP-n) has been studied by monitoring the disappearance yields and phosphorescence lifetimes of reactants.[2] BP-n shows methylene chain length dependence of the hydrogen abstraction rate in the triplet state similar to that of AQ-n mentioned above. In BP-n, the hydrogen abstraction rate of the benzophenone chromophore is 0.53×10^4 s^{-1} for $n=11$ and the increase is 0.46×10^4 s^{-1} per one additional methylene unit for $n>11$. When $n=14$, for example, the rates are 1×10^5 for AQ-14 and 0.18×10^5 s^{-1} for BP-14, respectively. Thus the rate constant of the former is about 5 times larger than that of the latter. The difference may be mainly attributable to the high reactivity of the anthraquinone triplet and partly to the existance of two reaction centers in the anthraquinone chromophore. Photochemical and photophysical similarity between AQ-n and BP-n implys that the photoreaction of AQ-n is conformationally controlled, in which conformational preequilibrium of the chain determines the reactivity, as theoretically analyzed for the latter.

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