Formation of Anthrahydroquinones (XAQH₂) *via* Excited Singlet Charge-transfer Complexes (or Singlet Ion Pairs) of Anthraquinones with 2,5-Dimethylhexa-2,4-diene (DMHD), and Photochemical Reaction of XAQH₂ with DMHD

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Upon picosecond excitation of a ground-state complex formed between anthraquinone (AQ, a typical planar molecule) and 2,5-dimethylhexa-2,4-diene (DMHD), an excited singlet charge-transfer complex [$^{1}(AQ^{\delta-} DMHD^{\delta+}$)*] or a singlet ion pair [¹(AQ⁺-DMHD⁺)] is produced within the duration of the excitation light pulse. This transient complex decays following a single-exponential function with a lifetime of 90 ps and the decay process is ascribed to the intracomplex proton transfer, yielding the semiquinone radical of AQ and the 2,5dimethylhexa-2,4-dienyl radical. A similar result has been obtained for non-planar 1,8-dichloroanthraquinone (cf. Hamanoue et al., J. Photochem. Photobiol. A: Chem., 1993, 76, 7), and so nanosecond laser photolysis of XAQ (anthraquinone or 1,8-dichloroanthraquinone) has also been performed and the second-order decay rate constant of the semiquinone radical (XAQH') of XAQ generated in DMHD-toluene is found to be one order of magnitude greater than that generated in ethanol without DMHD. Hence, it is concluded that XAQH* abstracts a hydrogen atom from the 2,5-dimethylhexa-2,4-dienyl radical yielding a photoreduced product (XAQH2, i.e. anthrahydroquinone or 1,8-dichloroanthrahydroquinone) and a biradical of DMHD; probably the reactions of this biradical yield the dimeric and oligomeric compounds of DMHD. Although steady-state photolysis of XAQ in neat DMHD causes the disappearance of the reactant absorption without the accompanying formation of XAQH₂, examination of the effect of DMHD concentration on the formation of XAQH₂ upon steady-state photolysis of XAQ in DMHD-toluene (or benzene) reveals that XAQH₂ disappears by its photochemical reaction with ground-state DMHD: For anthrahydroguinone, the formation of 4',4'-dimethyl-3'-(2-methylprop-1-en-1- yl)spiro[anthracene-10,2'-oxetan]-9(10H)-one is confirmed.

It is well known that the triplet-triplet energy transfer from a number of triplet sensitizers (such as aromatic carbonyl compounds and aromatic hydrocarbons) to 1,3-dienes occurs easily and that the triplet 1,3-dienes produced undergo efficient cis-trans isomerization and dimerization.¹⁻³ Based on the suggestion by Kochevar and Wagner⁴ and Caldwell et al.⁵ that triplet exciplexes (or excited triplet charge-transfer complexes) were the intermediates in the cis-trans isomerization of several alkenes photosensitized by triplet ketones, we performed picosecond 347.2 nm laser photolysis of 1,8dichloroanthraquinone (DCAQ, a non-planar molecule) in toluene containing 1 mol dm^{-3} of DMHD and observed the appearance of three transient absorption bands (A, B and C) which disappeared completely within a delay time of 1 ns.⁶ Although bands A ($\lambda_{max} = 543$ nm) and B ($\lambda_{max} = 508$ nm) were identical with the absorption bands due to the second (T_2) and lowest (T_1) excited triplet states of DCAQ, respectively, the spectral profile of band C ($\lambda_{max} = 610$ nm) was very similar to those of ionic species such as the radical anion $(DCAQ^{-})$ of DCAQ, a triplet exciplex [$^{3}(DCAQ-TEA)^{*}$] and a triplet ion pair [$^{3}(DCAQ^{-}-TEA^{+})$] of DCAQ⁻ with the radical cation (TEA⁺⁺) of triethylamine (TEA).⁷ Hence, band C was assigned to the absorption of a triplet exciplex (or an excited triplet charge-transfer complex) produced by the intermolecular electron transfer from ground-state DMHD to both the T_1 and T_2 states of DCAQ.

A ground-state complex is formed between DCAQ and DMHD, and selective excitation of this complex by 435 or 527 nm light pulses gives rise to the appearance of band C alone within the duration of the excitation light pulse.⁸ These results indicate that our previous assignment of band C is incorrect and that the transient species responsible for band C is an excited singlet charge-transfer complex [$^1(DCAQ^{\delta^-}-DMHD^{\delta^+})^*$] or a singlet ion pair [$^1(DCAQ^{-}-DMHD^{+})$]. As an extension of our study on the photophysics and photo-

chemistry of anthraquinone and its derivatives,⁶⁻¹³ this paper deals with (1) The formation and decay of an excited singlet charge-transfer complex (or a singlet ion pair) upon picosecond laser photolysis of AQ (a typical planar molecule) in DMHD-toluene and neat DMHD. (2) The decay process of the semiquinone radical (XAQH') yielding the corresponding anthrahydroquinone (XAQH₂) is examined by nanosecond laser photolysis of XAQ (AQ or DCAQ) in DMHD-toluene, because XAQH' produced in this mixed solvent decays following second-order reaction kinetics with a rate constant which is one order of magnitude greater than those of the semiguinone radicals of several anthraquinones generated in ethanol without DMHD. (3), The effect of DMHD concentration on the formation of XAQH₂ upon steady-state photolysis of XAQ in DMHD-toluene (or benzene) is examined, because the disappearance of the reactant absorption without the accompanying formation of $XAQH_2$ is observed in neat DMHD, while the presence of a small amount of DMHD in toluene (or benzene) enhances the formation of XAQH₂.

Experimental

The methods for purification of CP-grade AQ (Wako) and EP-grade DCAQ (Tokyo Kasei) have been given previously.⁹ Although spectral-grade benzene and scintillation-grade toluene from Dojin were used without further purification, spectral-grade ethanol (Nacarai) was dried using a 3A molecular sieves (Wako) preheated in a crucible over a Bunsen burner and cooled *in vacuo*, and DMHD (Aldrich) was distilled immediately before use. The sample solutions for steady-state photolysis and nanosecond laser photolysis were degassed by several freeze-pump-thaw cycles, while those for picosecond laser photolysis were not degassed.

All experiments were performed at room temperature, and steady-state photolysis was performed using the 366 or 405 nm monochromatic light selected from a USH-500D superhigh-pressure mercury lamp. The ground-state absorption spectra of DMHD, anthraquinones (AQ and DCAQ) and their photoreduced products (XAQH₂) were recorded by a Hitachi 200-20 spectrophotometer. To discover if the dimeric and oligomeric compounds formed via a biradical of DMHD which was generated by the hydrogen-atom abstraction of the semiquinone radical of AQ from the 2,5-dimethylhexa-2, 4-dienyl radical, DMHD solvent was removed after steadystate photolysis and the residual products were analysed by a Shimadzu QP-1000 GC-mass spectrometer. The photoproduct was separated by a Shimadzu QP-1000 GC-mass spectrometer. The photoproduct (produced by a photochemical reaction of anthrahydroquinone with DMHD) was separated by thin-layer chromatograpy using a silica gel plate (Merck) and hexane-methylchloride solvent (both Wako GR grade, in 1:1 volume ratio) and then analysed in ²H]chloroform (Wako) solvent using a ¹H NMR spectrometer (GM QE-300).

Nanosecond laser photolysis was carried out by the second harmonic (347.2 nm) from a Q-switched ruby laser, where the full width at the half-maximum intensity (FWHM) of the excitation light pulse was 20 ns and the transient absorption spectrum was recorded using a multichannel analyser controlled by a personal computer (NEC PC-9801RA).¹⁴ The decay curve of transient absorption with time was analysed by means of a combination of a photomultiplier (Hamamatsu Photonics R666) with a storage ocilloscope (Iwatsu TS-8123) controlled by the computer.

For picosecond laser photolysis, the second harmonic (347.2 nm, FWHM = 30 ps) from a mode-locked ruby laser was used as the excitation light pulse. By focusing this into acetonitrile, two Raman-scattering light pulses (435 and 502 nm) were also generated for sample excitation. As described later, we believe that the sample excitation is mainly caused by the 435 nm Raman-scattering light pulse. In the conventional picosecond absorption spectroscopy, two independent polychromator-image sensor detector systems are needed and the intensities of the probing and reference beams were measured separately, resulting in some variability for the derived

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absorbance spectrum.¹⁵ To perform the picosecond doublebeam absorption spectroscopy by simultaneous intensity measurements of the probing and reference beams using a single poly-chromator (Unisoku M200), we recently constructed a detector system composed of a dual linear image sensor (Hamamatsu Photonics S4801-512Q) controlled by a personal computer (NEC PC-9801Vm).¹⁶

Results and Discussion

Fig. 1 shows the transient absorption spectra obtained by picosecond 347.2 nm laser photolysis of AQ (1.2×10^{-3} mol dm^{-3}) in DMHD (1 mol dm^{-3})-toluene and neat DMHD. Although not shown in Fig. 1A, a triplet-triplet absorption band due to triplet AQ is observed around 400 nm in DMHD (1 mol dm^{-3})-toluene, even at a delay time of 0 ps. but no equivalent band is observed in neat DMHD. The transient absorption spectra in DMHD (1 mol dm⁻³)toluene obtained using the 435 nm light pulse (Raman scattering light pulse) also show no triplet-triplet band but are otherwise identical with those obtained using the 347.2 nm pulse. The results in neat DMHD are independent of the wavelength excitation. As shown in Fig. 2, irrespective of the excitation wavelength and the concentration of DMHD, the rise and decay of transient absorption with time (monitored at 575 nm) clearly reveal that band C builds up within the duration of the excitation light pulse and then decays following a single-exponential function with a lifetime of 90 ps; FWHM of the 435 nm Raman-scattering light pulse was assumed to be equal to that of the 347.2 nm second harmonic light pulse (30 ps). Hence, we suppose that a transient species responsible for band C is produced immediately after excitation of a ground-state complex $[^{1}(AQ-DMHD)_{G}]$ between AQ and DMHD. Band C can then be ascribed to the absorption of an excited singlet charge-transfer complex $[^{1}(AQ^{d}$ $DMHD^{\delta^+}$)*] or a singlet ion pair $[^1(AQ^{-}-DMHD^{+})]$, because its lifetime (90 ps) is very short compared with that of a triplet exciplex [³(AQ-TEA)*] or a triplet ion pair $[^{3}(AQ^{-}-TEA^{+})]$, *i.e.* 0.16 µs in toluene, 0.42 µs in ethanol or 0.09 μ s in acetonitrile each containing 0.2 mol dm⁻³ TEA.13



Fig. 1 Transient absorption spectra obtained by picosecond 347.2 nm laser photolysis of AQ $(1.2 \times 10^{-3} \text{ mol dm}^{-3})$ in, A, DMHD (1 mol dm⁻³)-toluene and, B, neat DMHD after (a) 0, (b) 40, (c) 100 ps and (d) 1 ns time delay; pathlength 2 mm



Fig. 2 Change in the relative absorbance (A_1/A_{max}) of band C (monitored at 575 nm) in the picosecond time regime: (\bullet) 347.2 nm excitation of AQ in DMHD (1 mol dm⁻³)-toluene; (\bigcirc) 347.2 nm excitation of AQ in neat DMHD; (\blacksquare) 435 nm excitation of AQ in DMHD (1 mol dm⁻³)-toluene. The full line is the best-fit curve calculated using an excitation pulse width (FWHM) of 30 ps and a lifetime of 90 ps.

The existence of the ground-state complex $[^{1}(AQ-DMHD)_{G}]$ is supported by the following reasons. (1) The ground-state absorption spectra shown in Fig. 3 reveal that the absorption intensity (>410 nm) of 3 mol dm^{-3} DMHD in toluene is very weak compared with that of 1.2×10^{-3} mol dm⁻³ AQ in toluene without DMHD and the sum of these two spectra cannot reproduce the spectrum of AQ $(1.2 \times 10^{-3} \text{ mol } \text{dm}^{-3})$ in DMHD (3 mol $\text{dm}^{-3})$ toluene, indicating the formation of ${}^{1}(AQ-DMHD)_{G}$. (2) Both free AQ and $(AQ-DMHD)_G$ are expected to exist in DMHD (1 mol dm⁻³)-toluene and so the 347.2 nm light pulse should excite both compounds. In fact, as stated previously, both band C and the triplet-triplet absorption band of AQ are observed in DMHD (1 mol dm⁻³)-toluene even at a time delay of 0 ps. Although the triplet-triplet absorption band of AQ is very similar to the band due to the semiquinone radical of AQ, this radical is generated at a much longer delay time, i.e. the absorption intensity due to the semiquinone radical at 0 ps delay is very weak as shown later (cf. Fig. 4). (3) In Fig. 3, a comparison of Raman-scattering light pulses with the ground-state absorption spectra of DMHD, AQ and $(AQ-DMHD)_G$ indicates that only



Fig. 3 Ground-state absorption spectra of AQ $(1.2 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$ in toluene with (a) 0, (b) 1 and (c) 3 mol dm⁻³ DMHD, and of DMHD (3 mol dm⁻³) in toluene (---) recorded using a toluene reference; pathlength 10 mm. Dotted lines show the spectral profiles and relative intensities of the Raman-scattering light pulses (435 and 502 nm).

 $^{1}(AQ-DMHD)_{G}$ can be excited by these pulses. In fact, the transient absorption due to triplet AQ is not observed even in DMHD (1 mol dm^{-3})-toluene. The intensities of the Raman-scattering light pulse and the sample absorption at 502 nm are very weak compared with those at 435 nm and so excitation of ${}^{1}(AQ-DMHD)_{G}$ may be caused mainly by the 435 nm pulse. (4) In neat DMHD, therefore, the appearance of only band C upon 347.2 or 435 nm excitation indicates the absence of free AQ. (5) As reported for DCAQ in the previous paper,⁸ not only band C but also the absorption bands due to the second (band A) and lowest (band B) excited triplet states of DCAQ can clearly be see upon 347.2 nm excitation of DCAQ in DMHD (1 mol dm⁻³)-toluene, but 435 nm excitation gives rise to the appearance of only band C, in spite of the presence of both free DCAQ and its complex with DMHD. Of course, 347.2 or 435 nm excitation of DCAQ in neat DMHD gives only band C.

For benzophenone (BP) in DMHD (1 mol dm^{-3})acetonitrile (or cyclohexane) or neat DMHD, the formation of a ground-state BP-DMHD complex has also been observed and excitation of this complex gives rise to the appearance of a transient absorption band ($\lambda_{max} = 565-570$ nm) due to an excited singlet charge-transfer complex $[^{1}(BP^{\delta} - DMHD.^{\delta^{+}})^{*}]$ or а singlet ion pair [¹(BP⁻⁻-DMHD⁺)] with a lifetime of 10 ps.¹⁷ During the decrease in the transient absorption band with time, no evidence supporting the accompanying formation of an excited triplet charge-transfer complex $[^{3}(BP^{\delta^{-}}-DMHD^{\delta^{+}})^{*}]$ or a triplet ion pair $[^{3}(BP^{*^{-}}-DMHD^{*^{+}})]$ is obtained. Neither the formation of the radical anion nor the ketyl radical of BP is observed. Hence, the decay process of ${}^{1}(BP^{\delta}-DMHD^{\delta})^{*}$ $[or (BP^{-}-DMHD^{+})]$ has been ascribed to the intracomplex back electron transfer (or the charge recombination) yielding the ground-state BP-DMHD complex and/or free $^{1}(AQ^{\delta-}-DMHD^{\delta+})^{*}$ plus BP DMHD. For For $^{1}(AQ^{-}-DMHD^{+})]$, however, the decrease of band C with time is accompanied by the increase of a new absorption (band D) as shown in Fig. 4. Moreover, the increase of band



Fig. 4 Appearance of band D upon picosecond 347.2 nm laser photolysis of AQ $(1.2 \times 10^{-3} \text{ mol dm}^{-3})$ in neat DMHD after (a) 0, (b) 40, (c) 100 ps and (d) 1 ns time delay; pathlength 2 mm





Fig. 5 Increase of band D monitored at 420 nm in the picosecond time regime. The full line is the calculated single-exponential rise curve.

RD with time (Fig. 5) can be analysed by a single-exponential function calculated using an excitation pulse width (FWHM) of 30 ps and a rise time of 90 ps. A similar result has also been obtained for non-planar DCAQ.⁸

Band D observed for XAQ (AQ or DCAQ) is identical with the absorption bands due to the semiquinone radicals of several anthraquinones.¹⁰ Hence, we conclude that the decay process of the excited singlet charge-transfer complex $[^{1}(XAQ^{\delta^{-}}-DMHD^{\delta^{+}})^{*}]$ or the singlet ion pair [1(XAQ^{•-}-DMHD^{•+})] obtained for XAQ is the intracomplex proton transfer yielding XAQH' and DMHD'. As shown in Fig. 6, the transient absorption spectrum obtained at the end of the nanosecond pulse excitation (40 ns delay) of XAQ in DMHD (1 mol dm^{-3})-toluene also reveals the appearance of band D, but the spectrum obtained at 2 ms delay is identiphotoreduced with of the cal that product (anthrahydroquinone or 1,8-dichloroanthrahydroquinone) as shown later (cf. Fig. 9, later). Moreover, Fig. 7 reveals that the decay curve of transient absorption with time (monitored at 380 nm) can be analysed by second-order reaction kinetics with a decay rate constant of $k_d = 8.6\varepsilon \times 10^5 \text{ dm}^5 \text{ mol}^{-1} \text{ s}^{-1}$



Fig. 7 Decay curve of the transient absorption at 380 nm (----) obtained by 347.2 nm nanosecond laser photolysis of (a) 1.2×10^{-3} mol dm⁻³ AQ and (b) 2×10^{-3} mol dm⁻³ DCAQ in DMHD (1 mol dm⁻³)-toluene; pathlength 10 mm. (---) Second-order decay curve calculated using $k_d = (a) 8.6\varepsilon \times 10^5$ and (b) $9.0\varepsilon \times 10^5$ dm³ mol⁻¹ s⁻¹, where ε is the molar absorption coefficient of XAQH^{*}.

or $k_d = 9.0\varepsilon \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the semiquinone radical of AQ or DCAQ, respectively, where ε is the molar absorption coefficient of XAQH[•]. These values of k_d are about one order of magnitude greater than those of the semiquinone radicals of several anthraquinones generated in ethanol without DMHD $[k_d = (5.3\varepsilon \times 10^4) - (1.1\varepsilon \times 10^5) \text{ dm}^3$ $mol^{-1} s^{-1}$], where the disproportionation reaction of two semiquinone radicals gives rise to the simultaneous formation of XAQH₂ (the corresponding anthrahydroquinone) and XAQ (the original anthraquinone).^{10,11} Hence, XAQH' generated via $(XAQ^{\delta}-DMHD^{\delta})*$ [or $(XAQ^{-}-DMHD^{+})$] may abstract a hydrogen atom from DMHD yielding XAQH₂ and a biradical of DMHD (DMHD"). In fact, the spectrum at 2 ms delay shown in Fig. 6 corresponds to the non-decay component of transient absorption shown in Fig. 7, i.e. the decay of band D with time is accompanied by the formation of XAQH₂. By GC-mass analysis of the photoproducts (obtained upon steady-state photolysis of AQ in neat DMHD) we have confirmed the existence of dimeric and oligomeric compounds which are probably formed via DMHD", based on the following reasons. (1) Formation of



Fig. 6 Absorption spectra obtained by 347.2 nm nanosecond laser photolysis of, A, 1.2×10^{-3} mol dm⁻³ AQ and, B, 2×10^{-3} mol dm⁻³ DCAQ in DMHD (1 mol dm⁻³)-toluene after (a) 40 ns and (b) 2 ms time delay; pathlength 10 mm



Fig. 8 Absorption spectral change upon 366 nm steady-state photolysis of (a) AQ for (top-bottom) 0, 4, 8, 15, 80 and 140 min, and (b) DCAQ for (top-bottom) 0, 6, 15, 25, 35 and 50 min (both 1.2×10^{-3} mol dm⁻³) in neat DMHD; pathlength 10 mm

these compounds by a reaction of triplet AQ with groundstate DMHD can be ruled out because free AQ does not exist in neat DMHD; (2) the yield of such dimeric and oligomeric compounds upon photolysis of DMHD alone or AQH_2 in neat DMHD is negligibly small.

If our conclusion stated above is correct, steady-state photolysis of XAQ (AQ or DCAQ) in neat DMHD should give rise to the formation of $XAQH_2$ via $XAQH^*$ generated by the intracomplex proton transfer in ${}^{1}(XAQ^{\delta^-}-DMHD^{\delta^+})^*$ [or ¹(XAQ⁻⁻-DMHD⁺)], because only the ground-state XAQ-DMHD complex exists in neat DMHD and picosecond laser photolysis of this sample solution populates only ${}^{1}(XAQ^{\delta} -$ DMHD³⁺)* [or ¹XAQ^{•-}-DMHD^{•+})], *i.e.* no triplet XAQ is populated. In contrast, as shown in Fig. 8, steady-state photolysis of XAQ in neat DMHD reveals no formation of XAQH₂. As shown in Fig. 9(a), (b), (e) and (f), however, one can clearly observe that steady-state photolysis of XAQ in toluene (without DMHD) gives rise to the appearance of an absorption band due to XAQH₂ and the formation of XAQH₂ is enhanced by the addition of 1.5×10^{-3} mol dm⁻³ DMHD. In toluene without DMHD, XAQH₂ is produced via the semiquinone radical generated by the hydrogen-atom abstraction of triplet XAQ from the solvent.^{10,11} Such a DMHD-enhanced formation of XAQH₂ is more clearly seen in benzene, as shown in Fig. 9(c), (d), (g) and (h), because the

hydrogen-atom abstraction of triplet XAQ from toluene occurs easily compared with that from benzene. Therefore, we have measured the absorbance (at 400 nm for AQ or 410 nm for DCAQ) before (A_0) and after (A_t) steady-state photolysis of XAQ in DMHD (0–1 mol dm⁻³)-benzene, and a plot of A_t/A_0 against photolysis time reveals that the formation of XAQH₂ is enhanced upon addition of DMHD up to 0.05 mol dm⁻³, as shown in Fig. 10(a) and (c). At a much higher concentration of DMHD, however, the formation of XAQH₂ is retarded, as shown in Fig. 10(b) and (d).

The spectra shown by the full lines in Fig. 11(a) indicate the formation of AQH₂ upon 368 nm steady-state photolysis of AQ in toluene without DMHD. After photolysis, changing the solvent to DMHD *in vacuo* causes a small spectral decrease as shown by the dashed line, and further photolysis causes the disappearance of the absorption spectrum due to AQH₂ [cf. Fig. 11(b)]. To obtain a high yield of AQH₂, 366 nm steady-state photolysis of AQ in ethanol without DMHD was also performed before changing the solvent to DMHD *in vacuo* and performing 405 nm steady-state photolysis. We have found that the absorption spectrum of AQH₂ disappears but that the final product in this solution is identical with that produced upon 366 nm steady-state photolysis of AQ in neat DMHD. This result indicates that AQH₂ disappears by its photochemical reaction with ground-state



Fig. 9 Formation of XAQH₂ upon 366 nm steady-state photolysis of, A, AQ and, B, DCAQ (both $0.3 \times 10^{-3} \text{ mol } \text{dm}^{-3}$) in (a), (e) DMHD (1.5 × $10^{-3} \text{ mol } \text{dm}^{-3}$)-toluene, (b), (f) toluene, (c), (g) DMHD ($1.5 \times 10^{-3} \text{ mol } \text{dm}^{-3}$)-benzene and (d), (h) benzene at increasing times (indicated by arrows) of (a), (b) 0, 1, 2, 3, 6; (c) 0, 6, 15, 30, 60; (d) 0, 10, 20, 40, 80; (e) 0, 1, 2, 4, 8; (f) 0, 2, 4, 6, 8; (g) 0, 1, 2, 3.5, 7.5; and (h) 0, 40, 90, 120, 180 min.

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Fig. 10 Change in the relative absorbance (A_d/A_0) at, A, 400 nm for AQ and, B, 410 nm for DCAQ during 366 nm steady-state photolysis of XAQ $(1.2 \times 10^{-3} \text{ mol dm}^{-3})$ in benzene containing (a), $(c) \square$, $0; \blacktriangle$, $0.001; \triangle$, $0.005; \oplus$, $0.01; \bigcirc$, 0.05 and (b), $(d) \bigcirc$, $0.05; \oplus$, $0.1; \triangle$, $0.5; \square$, 1 mol dm⁻³ DMHD; pathlength 10 mm

DMHD. We propose that the final product produced by a photochemical reaction of anthrahydroquinone with DMHD is 4',4'-dimethyl-3'-(2-methylprop-1-en-1-yl)spiro[anthracene-10,2'-oxetan]-9(10H)-one, shown by the following structure,



because, in comparison with the results reported for several oxetanes,^{18,19} the ¹H NMR signals obtained for the final product can be assigned as follows: $\delta = 8.21$ [1 H, dd, J 7.8, 0.9, H(5)], 8.1 [3 H, m, H(1, 4, 8)], 7.68 [1 H, td, J 7.5, 1.5, H(6)], 7.63 [1 H, td, J 7.8, 1.5, H(3)], 7.44 [2 H, t(broad), J 7.5, H(2,7)], 5.45 [1 H, d(broad), J 9.9, =CH], 3.53 [1 H, d, J 9.9, C(3)—H of oxetane ring], 1.75 [3 H, s, Me(1) or Me(2)], 1.56 [3 H, s, Me(2) or Me(1)], 1.39 [3 H, s(broad), Me(3) or Me(4)] and 1.24 ppm [3 H, J 1.2, Me(4) or Me(3)] (J in H_z).

In summary, the overall photochemistry of planar AQ (or non-planar DCAQ) in the presence of DMHD can be interpreted as follows:



(1) In neat DMHD, all molecules of XAQ form the groundstate complex $[^{1}(XAQ-DMHD)_{G}]$ and excitation of this complex by the 347.2 nm (or the 435 nm) light pulse populates only the excited singlet charge-transfer complex $[^{1}(XAQ^{\delta^{-}}-DMHD^{\delta^{+}})^{*}]$ or the singlet ion pair $[^{1}(XAQ^{\cdot^{-}}-DMHD^{\cdot^{+}})]$ which is followed by the intracomplex proton transfer generating XAQH^{*} and DMHD^{*}. Although the hydrogen-atom abstraction of XAQH^{\cdot} from DMHD^{\cdot} yields XAQH₂ and the dimeric (and oligomeric) products which are formed by reactions of the biradical of DMHD, XAQH₂ disappears by its photochemical reaction with DMHD. The final product for AQH₂ is 4',4'-dimethyl-3'-(2-methylprop-1-en-1-yl)spiro [anthracene-10,2'-oxetan]-



Fig. 11 (a) Formation of AQH₂ upon 366 nm steady-state photolysis of AQ $(1.2 \times 10^{-3} \text{ mol dm}^{-3})$ in toluene (----) for 0, 1, 2, 3, 5 and 9 min (indicated by arrow) and after changing the solvent to DMHD in vacuo after photolysis (---). (b) Decrease in the absorption spectrum upon 366 nm steady-state photolysis of AQH₂ in neat DMHD for 0, 1, 2, 3.5, 6.5 and 16.5 min (indicated by arrow). (a), (b) Pathlength 10 mm.

9(10H)-one but that for $DCAQH_2$ is unknown owing to its complicated photochemical reactions, even in the absence of DMHD.¹¹ (2) In DMHD (1 mol dm⁻³)-toluene, both free XAQ and ¹(XAQ-DMHD)_G exist, and 347.2 nm picosecond laser photolysis of this sample solution gives rise to the formation of not only the lowest excited triplet state (³XAQ^{*}) [via the lowest excited singlet state (1XAQ*) of XAQ] but also ${}^{1}(XAQ^{\delta}-DMHD^{\delta})^{*}$ [or ${}^{1}(XAQ^{*}-DMHD^{*+})$]. 435 nm picosecond laser photolysis of this sample solution yields only ${}^{1}(XAQ^{\delta} - DMHD^{\delta})^{*}$ [or ${}^{1}(XAQ^{-} - DMHD^{+})$]. (3) Since steady-state photolysis of XAQ in toluene (or benzene) without DMHD yields XAQH₂, ³XAQ* populated by 347.2 nm excitation of free XAQ undergoes a usual photochemical reaction,^{10,11} i.e. ³XAQ* abstracts a hydrogen atom from toluene (or benzene) yielding XAQH' which is followed by a disproportionation reaction of two XAQH' giving rise to the simultaneous formation of XAQH₂ and XAQ. Although ³XAQ* is quenched by DMHD with a quenching rate constant of 4.0×10^9 dm³ mol⁻¹ s⁻¹ for triplet AQ or 2.6×10^9 $dm^3 mol^{-1} s^{-1}$ for triplet DCAQ, no evidence supporting the formation of XAQH₂ via the semiquinone radical generated by the hydrogen-atom abstraction of ³XAQ* from DMHD has been obtained.

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