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PHOTOREDUCTION OF ANTHRAQUINONE IN AQUEOUS MICELLAR SOLUTION

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Summary

Anthraquinol and surfactant–anthrahydroquinone ether are the major products of the UV photolysis of anthraquinone (AQ) in aqueous sodium dodecyl sulphate solution. Photoreduction of the triplet state of AQ by the surfactant alkyl chain is followed by a radical pair reaction which is either recombination or hydrogen abstraction. The photochemistry of AQ in micellar solution is compared with the results of the steady state photolysis and the laser photolysis of AQ in *n*-dodecane and other non-aqueous solvents.

1. Introduction

The photolysis of anthraquinone (AQ) has been studied in homogeneous solutions of various solvents [1 - 9]. The primary step in the photolysis is the abstraction of a hydrogen atom from the solvent molecule by an excited state of AQ, usually the triplet state [9 - 11]. The subsequent fate of the radical pair depends upon the solvent. The radical pair is usually separated in the process of spin relaxation and the re-encounter probability is small. Thus the photolysis of AQ in homogeneous solvents favours the disproportionation of $AQH^{\cdot}$ which regenerates AQ [3 - 7] and anthraquinol (AQH_2):

$$2AQH^{\cdot} \rightarrow AQH_2 + AQ \qquad (1)$$

or other reactions [4, 8]. In this work we report on a study of the photolysis of AQ in aqueous micellar solution. The distribution of AQ as one molecule per micelle prevents permanent separation of the radical pair after its formation, thereby excluding such reactions as reaction (1). In the micellar cage the radical pair reacts either by recombination or by hydrogen abstraction.

2. Experimental

AQ (Eastman Organic Chemicals) was recrystallized three times from benzene. Sodium dodecyl sulphate (SDS) (Koch-Light Lab.) was washed

with *n*-pentane and recrystallized four times from spectrograde methanol (Sarabhai Chemicals). *n*-Hexane (Merck, Spectrograde) and *n*-dodecane (J. T. Baker) were used as received without further purification. Other solvents used were of either AnalaR or Spectrograde quality. An aqueous micellar solution of AQ was prepared by stirring AQ (5×10^{-5} M) in a 0.1 M solution of SDS in distilled water at 70 - 80 °C for 3 - 4 h. Samples were degassed by nitrogen purging or by freeze–pump–thaw cycles on a vacuum line.

Absorption spectra were recorded using a Cary-17D spectrophotometer. Photolysis experiments were carried out using a low pressure mercury lamp (Phillips) fitted with a Corning CS-7-54 UV filter. Low excitation intensity was used for measuring the rate of photolysis and for fluorescence spectral recordings. Fluorescence lifetime measurements and the laser photolysis were performed using an N_2 laser (200 μJ, 7 ns) (AVCO EVERETT) operating at 50 - 100 pulses s^{-1}.

The separation of surfactant-bound and surfactant-free products after photolysis of AQ in the micellar solution was carried out using the following procedure. The photolysed sample was exposed to air for 1 h. Water was removed by vacuum evaporation. Surfactant-free products were removed from the solid by extraction with *n*-pentane or *n*-dodecane. The surfactant-bound products present together with the SDS were dried on a vacuum line.

3. Results

Photoreduction of AQ in the micellar solution was studied by absorption spectral changes which indicate the depletion of AQ and the build-up of products during photolysis. Curve a in Fig. 1 shows the absorption spectrum of AQ (5×10^{-5} M) in a degassed aqueous solution of SDS (0.1 M). Structureless absorption peaks are observed at 253, 274 and 325 nm. UV irradiation (300 - 400 nm) excites AQ ($\pi-\pi^*$ transition) and, upon continuous UV irradiation, the absorbance at 253 nm (and 325 nm) decreases indicating the depletion of AQ in the solution. The completion of the photolysis of AQ is indicated by the absence of any further decrease in the absorbances at 253 and 325 nm. Curve b in Fig. 1 shows the absorption spectrum of the products when AQ is completely photolysed (an irradiation time of 90 s). A prominent absorption peak at 267 nm and sharp and broad absorption peaks at 372 and 400 nm respectively are observed in the absorption spectrum of the products.

The rate of photolysis at reduced excitation light intensity was measured from the decrease in the absorbances at 253 and 325 nm. Figure 2 shows the percentage decrease in AQ as a function of the irradiation time in the photolysis of a degassed solution of AQ in micellar solution (curve a), in the presence of oxygen in a non-degassed solution of AQ in micellar solution (curve b) and in the presence of a paramagnetic additive $MnCl_2$ (5×10^{-2} M) in a degassed solution of AQ in micellar solution (curve c). The rate of photolysis is nearly constant in the initial phase of photolysis (up to 10%

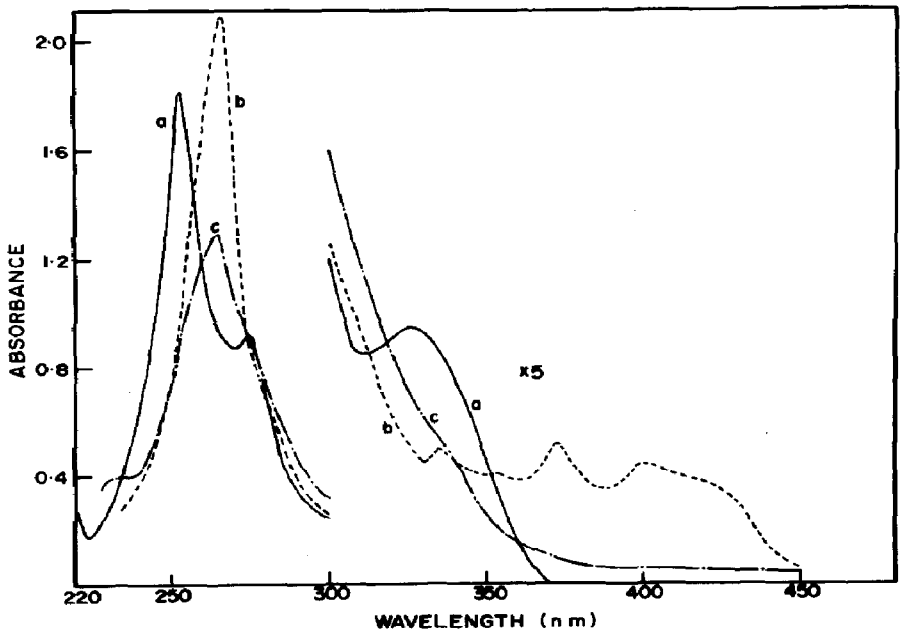

Fig. 1. Absorption spectra of AQ (5×10^{-5} M) in degassed aqueous SDS (0.1 M): curve a, AQ; curve b, after UV irradiation for 90 s; curve c, after remaining for 1 h in the dark.

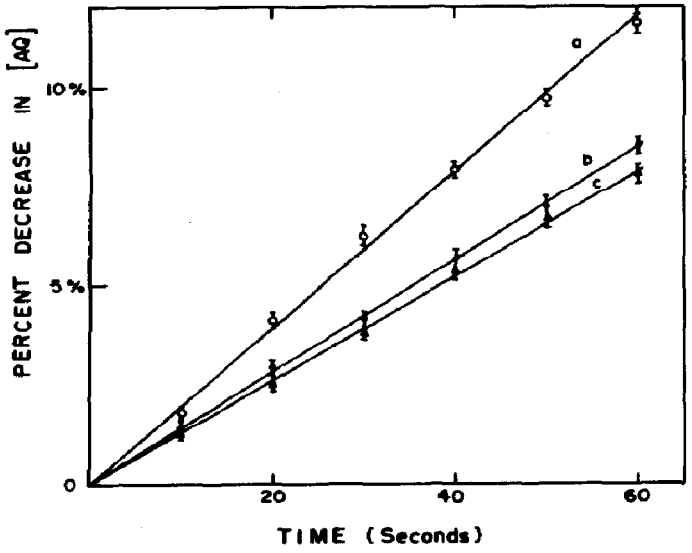

Fig. 2. Percentage decreases in the concentration of AQ (5×10^{-5} M) in the micellar solution as a function of the UV irradiation time: curve a, in the absence of additives; curve b, in the presence of oxygen (air); curve c, in the presence of $MnCl_2$ (5×10^{-2} M).

decrease in AQ) and thereafter the rate decreases owing to the depletion of AQ in the solution. The reduction in the rate of photolysis in the presence of O_2 or Mn^{2+} is consistent with the involvement of the triplet excited state of AQ in the photoreaction.

The absorption spectrum of the photolysed solution (curve b in Fig. 1) changed with time without further photolysis. Curve c in Fig. 1 shows the absorption spectrum of the photolysed sample after 60 min in the dark. This slow reaction is attributed to a surfactant-bound product, anthrahydroquinone ether of SDS, undergoing enol → keto isomerization (see later).

Figure 3 shows the fluorescence spectrum of the products immediately after photolysis of AQ in the micellar solution. Broad fluorescence emissions in the region 450 - 520 nm and at 410 nm are observed. The fluorescence intensity in the region 450 - 520 nm decreased with time. This slow dark reaction is observed in the surfactant-bound product (after separation from surfactant-free products) and is attributed to enol → keto isomerization (see later). The fluorescence spectra of AQH_2 and the surfactant-bound product in methanol are shown in Fig. 3 for comparison. The broad emission in the region 450 - 520 nm is attributed to AQH_2 and surfactant–anthrahydroquinone ether. The product(s) fluorescing at 410 nm is not identified.

The formation of AQH_2 as one of the products in the photolysis of AQ in micellar solution was confirmed by its reaction with oxygen on exposure to air. The absorption spectrum of the photoproducts (curve b in Fig. 1) showed a "prompt" decrease in the absorption at 267 nm (decrease of AQH_2) and a "prompt" increase in the absorptions at 253 and 325 nm due to the formation of AQ. The fluorescence intensity of the photoproducts also showed a "prompt" decrease on exposure to air. The amount of AQH_2 formed in the photolysis was estimated from the amount of surfactant-free AQ present in the *n*-pentane (or *n*-dodecane) extraction. The yield of AQH_2

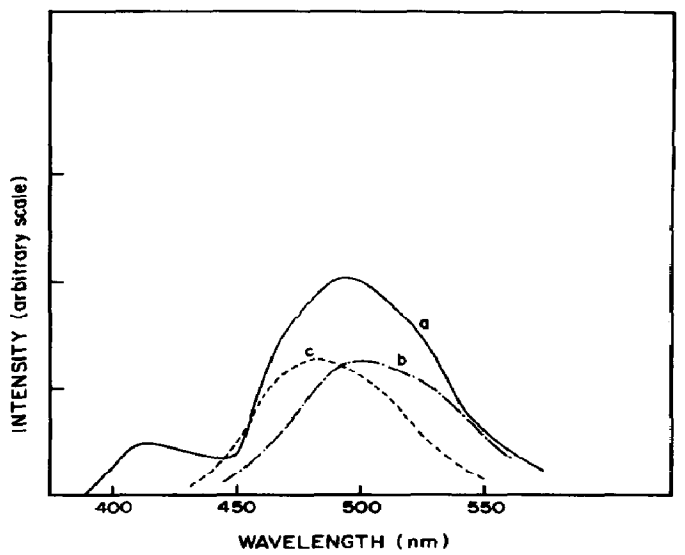

Fig. 3. Fluorescence spectra: curve a, the photolysis products of AQ (5×10^{-5} M) in micellar solution; curve b, the surfactant–anthrahydroquinone ether in methanol regenerated from the non-fluorescent surfactant-bound product by UV irradiation (see text); curve c, AQH_2 in methanol.

was 0.12 ± 0.02. This yield was unchanged when the irradiation time was changed from 90 to 180 s, indicating the completion of the photolysis of AQ in 90 s.

The isolated surfactant-bound product showed intense fluorescence at 495 nm (Fig. 3, curve b) when a degassed solution in methanol or in micellar solution was UV irradiated for 60 s. The absorption spectrum showed spectral features which are similar to those of AQH_2, suggesting that the fluorescing surfactant-bound product is surfactant–anthrahydroquinone ether. Figure 4 shows the absorption spectra of surfactant–anthrahydroquinone ether and AQH_2 (partially converted from AQ by UV irradiation) in degassed alkaline methanol (NaOH, 0.025 M).

The isomerization of the surfactant–anthrahydroquinone ether to the keto form is a slow dark reaction. In a thoroughly degassed micellar solution, the isomerization of surfactant–anthrahydroquinone ether follows first order kinetics with a rate constant of 7×10^{-5} s^{-1}. In the presence of oxygen (air) the rate constant increases to 10^{-3} s^{-1}.

Further, surfactant-free AQ can be recovered from the surfactant-bound product by photooxidation in alkaline methanol. Curve b in Fig. 4 shows the absorption spectrum of the surfactant-bound product in non-degassed methanol (0.025 M NaOH) after UV irradiation for 5 min. The absorption peaks at 252, 274 (shoulder) and 325 nm are characteristic of AQ. AQ can be extracted with *n*-pentane after evaporating the methanol, showing that

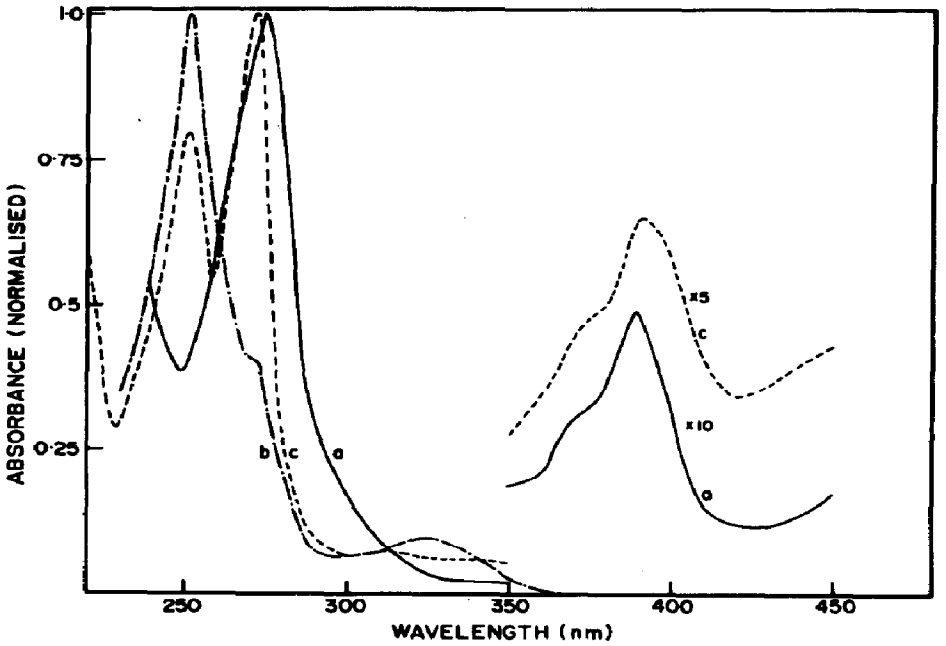

Fig. 4. Absorption spectra: curve a, the surfactant-bound product in degassed methanol (NaOH, 0.025 M) after UV irradiation for 60 s; curve b, the surfactant-bound product in non-degassed methanol (NaOH, 0.025 M) after UV irradiation for 5 min; curve c, AQ (252 nm) and AQH_2 (272.5 and 391 nm) in degassed alkaline methanol (NaOH, 0.025 M).

the recovered AQ is surfactant free. The yield of AQ thus recovered is 0.75 ± 0.05.

Photolyses of AQ in micellar solutions and in various solvents were performed using a high intensity UV source (N_2 laser pulse at 337.1 nm). The fluorescence emission of the photoproducts, excited by the laser pulse itself, is compared with the fluorescence emission of the products formed in low intensity UV photolysis. The fluorescence data in various solvents are summarized in Table 1.

Fluorescence emission in the region 450 - 520 nm is attributed to AQH_2 and anthrahydroquinone ether. Laser photolysis and low intensity photolysis produced identical fluorescence spectra in micellar solutions, *n*-dodecane and 2-propanol. In other solvents (except CCl_4) the low intensity photolysis produced no or weak fluorescence whereas laser photolysis produced strong fluorescence at 410 nm and in the region 450 - 520 nm. The photolysis of AQ in CCl_4 seems to follow a different path, as indicated by the completely different fluorescence spectrum of the products.

Fluorescence lifetime measurements were carried out in the laser photolysis experiments. The fluorescence lifetime in the 410 nm region was independent of wavelength and varied from 3 to 4 ns in the various solvents, including micellar solution. The fluorescence lifetime in the region 450 - 520 nm showed a marked wavelength dependence indicating the presence of at least two fluorescent products. The lifetime varied from 15 to 30 ns in the broad emission region. The fluorescence lifetime (32 ns) did not show any

TABLE 1

Fluorescence peaks/regions of the products of the photolysis of AQ in degassed solutions

Solvent	*Concentration* (M)	*Fluorescence peaks/regions* (nm)	
		Laser photolysis[a]	*Steady state*[b] *(low intensity)*
Micelle (SDS)	5×10^{-5}	410, 450 - 520	410, 450 - 520
n-Dodecane	5×10^{-4}	410, 450 - 520	410, 450 - 520
2-Propanol	1×10^{-3}	485[c]	485[c]
n-Hexane	5×10^{-4}	410, 430 - 520[d]	–
1,2-Dimethoxy-ethane (DME)	1.6×10^{-3}	410, 450 - 520	–
Benzene	1.6×10^{-3}	410, 450 - 520	–
CH_2Cl_2	1.5×10^{-3}	410, 450 - 520	–
$CHCl_3$	1.6×10^{-3}	400, 450 - 520	–
CCl_4[e]	1×10^{-3}	404, 427, 452, 496, 538	–

[a]Constant emission intensity after 60 s; total time, 5 min.
[b]Constant emission intensity after 2 min; total time, 5 min; –, weak or no fluorescence.
[c]AQH_2.
[d]Probably includes anthranol [8].
[e]Well-resolved fluorescence peaks in this solvent.

wavelength dependence in 2-propanol indicating that AQH_2 was the only product in the short-time photolysis of AQ in this solvent.

4. Discussion

In aqueous solutions the surfactant (SDS) molecules aggregate to form spherical micelles of approximate radius 20 Å. The concentration of the micelles in the solution is given by

$$[M] = \frac{[SDS] - CMC}{n} \tag{2}$$

where CMC is the critical micelle concentration (8×10^{-3} M for SDS) [12] and n is the aggregation number (approximately 60 for SDS) [13, 14]. The probability distribution of the solubilizate (AQ) among the micelles is given by the Poisson equation [15, 16]

$$P(x) = \frac{e^{-\mu}\mu^x}{x!} \tag{3}$$

where x is the occupancy number of the micelle and μ is the ratio of the number of solubilized AQ molecules to the number of micelles. In the micellar solution of AQ (5×10^{-5} M) in 0.1 M SDS ([M] $\approx 1.6 \times 10^{-3}$ M), $P(0) = 0.969$, $P(1) = 0.03$ and $P(\geq 2) = 6 \times 10^{-4}$. Thus 98% of the AQ molecules are distributed as one per micelle and the photoproducts originating from multiply occupied micelles are negligible.

The site of solubilization of AQ in the micelle may either be in the non-polar region (core of the micelle) or in the polar region near the inner surface of the micelle. The absorption spectrum of AQ in micellar solution is in close resemblance (*e.g.* spectral shifts and the absence of structure) to that of AQ in methanol rather than to that of AQ in *n*-dodecane. It is suggested that AQ is solubilized near the inner surface of the micelle where the local environment resembles [17] that of a polar solvent due to the penetration of water molecules. This is in agreement with nuclear magnetic resonance results [18] which show that benzoquinone and duroquinone are solubilized near the inner surface of the micelle. Although AQ is solubilized in the polar region containing water molecules, the photoreduction of AQ by water is inefficient. Steady state UV irradiation of a saturated solution of AQ (3×10^{-6} M) in water showed no change up to 10 min whereas under the same conditions the micellar solution of AQ was completely photolysed in 90 s.

Photolysis of AQ is initiated by the abstraction of a hydrogen atom by the excited state of AQ from an available hydrogen donor which, in the micellar phase, is the alkyl chain of the surfactant molecule. The reduction in the rate of photolysis of AQ in the presence of paramagnetic triplet quenchers such as O_2 or Mn^{2+} implies that the triplet state of AQ is involved in the hydrogen abstraction. The primary product of the photoreduction of ^3AQ is therefore a free radical pair in a triplet spin state:

$$^3AQ + SDS \longrightarrow {}^3(AQH^{\cdot} + SDS^{\cdot}) \quad (4)$$

Further reaction of the radical pair in the triplet spin state is unlikely because of spin restrictions which require that one of the products is formed in its energetically high triplet state. Dynamic motions of the free radicals induce spin rephasing [19], thus converting the triplet radical pair to a singlet radical pair which then reacts to give products in the singlet ground state. The probability of encounter of the free radicals after spin rephasing is greatly enhanced in a cage such as a micelle.

The formation of AQH_2 and the surfactant-bound product indicates that the singlet radical pair reacts either by hydrogen abstraction or by combination. We propose the following reaction scheme:

$$AQH^{\cdot} + SDS^{\cdot} \begin{cases} \longrightarrow AQH_2 + S\bar{D}S & (5) \\ \longrightarrow I & (6) \\ \longrightarrow \text{Other products} & (7) \end{cases}$$

where $S\bar{D}S$ is dehydrogenated SDS. The straight recombination of the two free radicals gives surfactant–anthrahydroquinone ether (I), whose spectral characteristics are likely to resemble those of AQH_2. Indeed, the absorption and emission spectra of the surfactant-bound product are in close resemblance to those of AQH_2 (Figs. 3 and 4).

The slow dark reaction ($k = 7 \times 10^{-5}$ s^{-1}) of I and the photoreversibility are attributed to enol → keto isomerization (see Fig. 5). The facile conversion of the surfactant-bound product to surfactant-free AQ in oxygen-containing alkaline methanol on UV irradiation is presumably the result of the (photo)-oxidation of I, which is stabilized as the enolate ion in an alkaline medium.

Apart from AQH_2 and I, we also observed products (surfactant free and surfactant bound) fluorescing at 410 nm in the photolysis of AQ in micellar solution. In the course of photolysis the fluorescence intensity at 410 nm grew to a maximum which coincided with the complete depletion of AQ; thereafter the fluorescence intensity remained constant. This observation means that the 410 nm product cannot originate from secondary photoreactions of I, II or AQH_2. It is suggested that the 410 nm product is formed directly in the radical pair reaction (7). The free-electron spin density in semiquinone radicals is maximum [20] at the oxygen atom and this explains

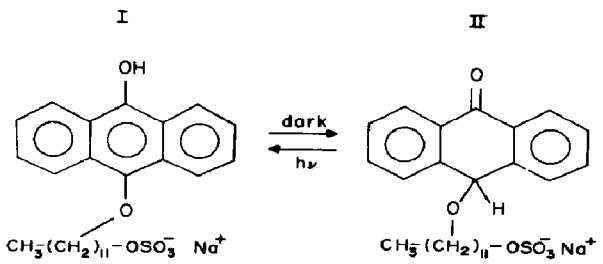

Fig. 5. The enol → keto isomerization of I.

the formation of AQH_2 and I resulting from oxygen-centred H$^{\cdot}$ abstraction or the recombination reaction of AQH$^{\cdot}$ and SDS$^{\cdot}$. It is possible that the non-zero spin density at other positions (carbon atoms) in AQH$^{\cdot}$ could lead to carbon-centred H$^{\cdot}$ abstraction or recombination. It is interesting to note that Hercules and Carlson [6] suggest similar structures, after ruling out several others, for an unidentified fluorescent 410 nm product formed in prolonged photolysis of AQH_2 in alcohol.

Fluorescence emission is observed in the pulsed laser photolysis of AQ in micellar solution and in other solvents (Table 1). The high photon density of the laser pulse (3.4×10^{14} photons pulse^{-1}) excites AQ in a small region of the sample (cross section of approximately 0.1 cm^2) and the photoreduction of ^{3}AQ occurs by H$^{\cdot}$ abstraction in the narrow laser excitation zone. The short pulse width (7 ns) of the laser pulse ensures that the primary products of the photoreduction, AQH$^{\cdot}$ and solvent free radicals (S$^{\cdot}$ or SDS$^{\cdot}$), are not excited by the same laser pulse. These free radicals will have reacted away before the arrival of the next laser pulse after an interval of 10 - 20 ms. The subsequent laser pulse excites AQ and the photoproducts formed from free radical reactions. The fluorescence intensity of the photoproducts reaches a maximum value with the establishment of an equilibrium concentration of AQ and its photoproducts within the excitation zone of the sample, brought about by the diffusion of these molecules in and out of the zone. Although the build-up of secondary photoproducts originating from AQH_2, I or the 410 nm product is possible, no appreciable change in the emission spectrum is observed for up to 5 min of photolysis time.

The laser photolysis of AQ in micellar solution leads to the products whose fluorescence spectrum is the same as that shown in Fig. 3 (curve a). As in the steady state low intensity photolysis, the free radicals are formed within the micellar cage and, subsequently, the radical pair reaction follows the same pathway (reactions (5), (6) and (7)). The fluorescence emission in the laser photolysis of AQ in micellar solution is attributable to AQH_2, I and the 410 nm product.

In the photolysis of AQ in homogeneous solutions, the initial formation of a radical pair may be followed by permanent separation without re-encounter. The separated free radicals are quenched in side reactions or in random reactive encounters such as the following:

$$2AQH^{\cdot} \longrightarrow \text{Products} \qquad (1)$$

$$2S^{\cdot} \longrightarrow \text{Products}$$

or

$$AQH^{\cdot} + S^{\cdot} \longrightarrow \text{Products}$$

The observation of fluorescent products originating from radical pair reactions in a homogeneous solution is more favourable in a highly viscous solution (which prevents radical pair separation) or in a concentrated solution at high exciting photon density. Thus in *n*-dodecane (η = 1.35 cP) even low intensity photolysis of AQ produces fluorescence emission (Table 1), whereas

in the less viscous *n*-hexane (η = 0.294 cP) solution intense fluorescence emission is observed only in laser photolysis. Similar fluorescence emissions attributable to AQH_2, anthrahydroquinone ether and the 410 nm product are observed in the laser photolysis of AQ in DME, benzene, CH_2Cl_2 and $CHCl_3$. In 2-propanol the low intensity photolysis or the laser photolysis of AQ produces fluorescence emission that is attributable to AQH_2 only. In this solvent efficient radical pair reaction occurs without separation and the radical pair reaction mechanism [3, 4] exclusively favours the formation of AQH_2. The well-resolved fluorescence emission peaks (Table 1) and wavelength-dependent fluorescence lifetimes in CCl_4 show that photolysis of AQ in this solvent follows a different pathway, one not initiated by hydrogen abstraction by ^3AQ.

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