Photochemistry in Micellar System. II. Photochemical Reduction of β-Arylquinonesulfonates in the Presence of Cationic Surfactants.[1]

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The photochemical reduction of sodium 9,10-phenanthraquinone-3-sulfonate (PQ) and sodium 1,2-naphthoquinone-4-sulfonate (NQ) to the corresponding diols has been studied in water containing cationic surfactants. Photoreduction of PQ was markedly accelerated in the presence of cationic surfactants whereas that of NQ was highly retarded. Both the acceleration and retardation of the photoreaction of these quinonesulfonates in the presence of cationic surfactants are explained as due to the formation of association complexes betwen the quinones and the surfactants.

The chemistry in heterogeneous systems is important in relation to that of biological systems. The rates of many bimolecular reactions have been found to be considerably affected in the presence of surfactant micelles which provide a convenient heterogeneous model system.[2-4] These micellar effects are generally explained in terms of the solubilization of substrate into the micellar interior, where the electrostatic or hydrophobic interaction between substrate, reactant and micelles is so large that the rate of reaction is modified. In the case of photochemical reaction, the nature of photoexcited state of the substrate would also be modified when it is solubilized into apolar micellar interior. The micellar catalysis in photochemical reactions is expected to be large than that in thermal reactions. Hautala and Letsinger have found that the nucleophilic substitution of 4-methoxy-1-nitronaphthalene with cyanide ion is enhanced by a factor of about 6800 by the addition of cetyltrimethylammonium chloride (CTACl);[5] the enhancement factor is unexpectedly large in comparison with that of the micellar effects in thermal reactions.[2-4]

We reported that the photochemically generated radical anions of 9,10-anthraquinonesulfonates are remarkably stabilized in the presence of either anionic or non-ionic surfactant.[6] We have investigated the photochemistry of β-arylquinonesulfonates in water containing various surfactants and the results are given in this paper. In the case of sodium 9,10-phenanthraquinone-3-sulfonate (PQ), the photoreduction was enhanced by the cationic surfactants, neither anionic nor non-ionic ones having any effect at all. The photoreduction of sodium 1,2-naphthoquinone-4-sulfonate (NQ), on the other hand, was highly retarded by cationic surfactants in comparison with that in pure water.[7] These effects of surfactants were recognized even at a concentration far below the critical micelle concentrations (CMC) of the surfactants. The formation of association complexes between the β-arylquinonesulfonates and the cationic surfactants was suggested to account for the experimental observation.

Experimental

Spectroscopic measurements were made with a Shimadzu UV-200 recording spectrometer, a Bruker WH-90 FT NMR spectrometer (90 MHz) and a JEOL JES-ME-3X ESR spectrometer (X-band).

Materials. PQ was prepared according to the procedure given by Werner.[8] Reagent grade NQ (Tokyo Kasei Kogyo Co. Ltd.) was further purified by recrystallization from aqueous methanol. Cetyltrimethylammonium bromide (CTABr) and chloride (CTACl) were recrystallized from water and methanol, respectively. Water was distilled and deionized with a column of ion-exchange resin.

Irradiation. The solution in a pyrex tube (ϕ 15 mm) was irradiated with a Riko 100W high-pressure mercury lamp combined with a Riko rotary photolysis apparatus RH400-10W at room temperature. The photolysis was undertaken under the aerobic conditions unless otherwise stated.

Quantum Yield. Monochromatic light was isolated from a Ushio 500W super high-pressure mercury arc USH-500D either with a combination filter of a Toshiba UV-D25, an aqueous nickel sulfate solution, and a glass plate (313 nm) or with a combination filter of a Toshiba UV-D1C and a UV-35 (365 nm). The light intensity was determined with a potassium ferrioxalate actinometer.

Results

Photolysis of PQ and NQ. NQ in water is photoreduced to sodium 1,2-dihydroxynaphthalene-4-sulfonate (NQH_2).[7] The quantum yield for the disappearance of NQ was determined to be 0.118±0.007 (pH 6.80). On the other hand, PQ in an aerobic phosphate buffer (pH 6.80) is considerably stable against irradiation. The quantum yield for the disappearance of PQ ($[PQ]_0=1.0\times10^{-3}$ M) at 313 nm is $(5.5\pm1.5)\times10^{-4}$. Under the unaerobic conditions, the photolysis of PQ is accelerated about two-fold, no photoproducts being identified by UV spectra. The photolysis of PQ (5.0×10^{-4} M) is markedly accelerated, however, in the presence of CTABr (4.0×10^{-3} M). Upon irradiation, new absorption bands appear at 232, 254, 258, 275, and 318 nm, the intensities of the absorption due to PQ at 260, 264, 324, and 416 nm decreasing. The spectrum of the photoproduct is in complete agreement with that of the authentic sample of sodium 9,10-dihydroxyphenanthrene-3-sulfonate (PQH_2) prepared by the zinc dust-hydrochloric acid reduction. The isosbestic points are observed at 262, 283, and 327 nm up to the 70% conversion. The quantum yield for the disappearance of PQ ($[PQ]_0=1.0\times10^{-3}$ M) in the presence of CTABr (4.0×10^{-3} M) is $(1.3\pm0.1)\times10^{-2}$. CTACl (4.0×10^{-3} M) catalyzes the photoreduction more effectively than CTABr ($\phi_{CTACl}/\phi_{CTABr}=2.3$).

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Unlike the case of PQ, the photoreduction of NQ (5.0×10^{-4} M) in water is highly retarded in the presence of CTACl (5.0×10^{-3} M) ($\phi_{\mathrm{CTACl}}/\phi_0=0.076$). Since the photoreduction of NQ in water is not affected by the addition of Cl$^-$ (2.0×10^{-3} M) ($\phi_{\mathrm{NaCl}}/\phi_0=0.99$) in contrast to the case of Br$^-$ ($\phi_{\mathrm{KBr}}/\phi_0=0.45$), the retarding effect of CTACl should be ascribed to the binding of NQ with the surfactant.

Photoreaction of either PQ or NQ is not affected by the addition of anionic (sodium lauryl sulfate) or nonionic (polysorbate 80) surfactant above the CMC.

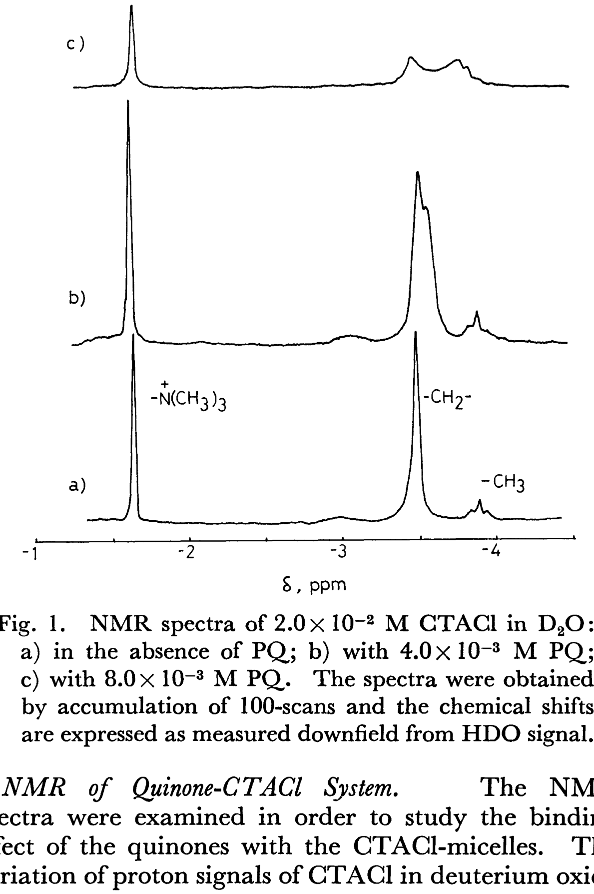

Fig. 1. NMR spectra of 2.0×10^{-2} M CTACl in D_2O: a) in the absence of PQ; b) with 4.0×10^{-3} M PQ; c) with 8.0×10^{-3} M PQ. The spectra were obtained by accumulation of 100-scans and the chemical shifts are expressed as measured downfield from HDO signal.

NMR of Quinone-CTACl System. The NMR spectra were examined in order to study the binding effect of the quinones with the CTACl-micelles. The variation of proton signals of CTACl in deuterium oxide with the concentration of PQ is shown in Fig. 1. The signals of $(CH_3)_3N^+$ and terminal $-CH_3$ protons are scarcely affected by the addition of PQ. As to the methylene protons, a part of the signal is shifted so that partially resolved two peaks are observed on the addition of PQ. At higher concentration of PQ, about a half of the methylene proton signals are shifted upfield, all the spectra showing considerable broadening due to the increased viscosity of the CTACl solution. Bunton studied the effects of added sodium alkylbenzenesulfonates on the proton signals of CTABr above the CMC and found appreciable broadening and upfield shift of the $(CH_3)_3N^+$ proton signals;[9] the methylene proton signals are separated into two groups, one shifted upfield and the other downfield. Bunton thus suggested that the phenyl group is inserted into the micelles so that the sulfonate group is in the aqueous environment (Fig. 2a). In the present experiment, the NMR spectra of the PQ-CTACl indicates that the $(CH_3)_3N^+$ protons are not affected by the magnetic anisotropy of the aromatic ring.

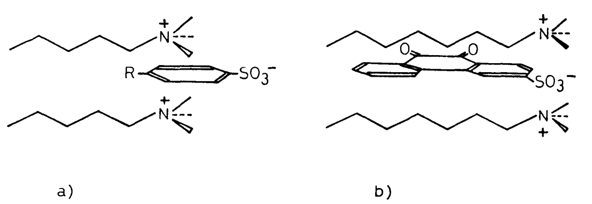

Fig. 2. Models of the binding of anionic substrates with cationic micelles: a) alkylbenzenesulfonate-CTABr; b) PQ-CTACl.

The SO_3^- group of PQ is considered to be associated with the $(CH_3)_3N^+$ of the surfactant so that the aromatic ring is incorporated into the hydrophobic micelle core (Fig. 2b).

Essentially the same results were obtained with the NQ-CTACl system.

Effect of Surfactant Concentration. If the effects of cationic surfactants on the photoreductions are due to the ordinary micellar effects, both the acceleration (PQ) and retardation (NQ) should become appreciable as the concentrations of the surfactants exceed the CMC. The effect of CTABr concentration on the photoreduction rate of PQ is shown in Fig. 3. Since the CMC generally decreases on the addition of inorganic salts,[2-4] the experiments were carried out in non-buffered system (pH *ca.* 5.8). As shown in Fig. 3, the rate of photoreduction is significantly enhanced at the concentration of CTABr far below the CMC ($\sim10^{-3}$ M).[2] The onset of sharp decrease in the reaction rate of NQ was also located at CTACl concentration below the CMC (Fig. 3).[10] Further addition of surfactants above the CMC gave no effect on the photoreduction of either PQ or NQ. The results suggest that the effects of the cationic surfactants on the photoreactions of these β-arylquinonesulfonates are not attributed to the ordinary micellar effects. A similar effect of CTABr was observed in the fluorescent probe experiments with 8-toluidinyl-1-naphthalenesulfonate where the fluorescent yield is enhanced in the presence of CTABr below the CMC.[11]

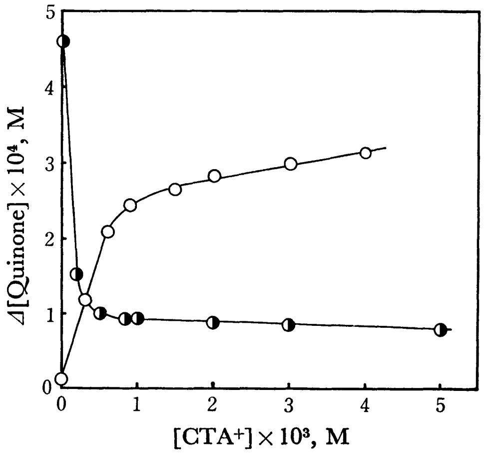

Fig. 3. The effect of cationic surfactant concentration on the β-arylquinones photochemistry. The aerobic aqueous solutions of PQ (—○—) and NQ (—◐—) (5.0×10^{-4} M) were irradiated for 15 and 2 min, respectively, at room temperature.

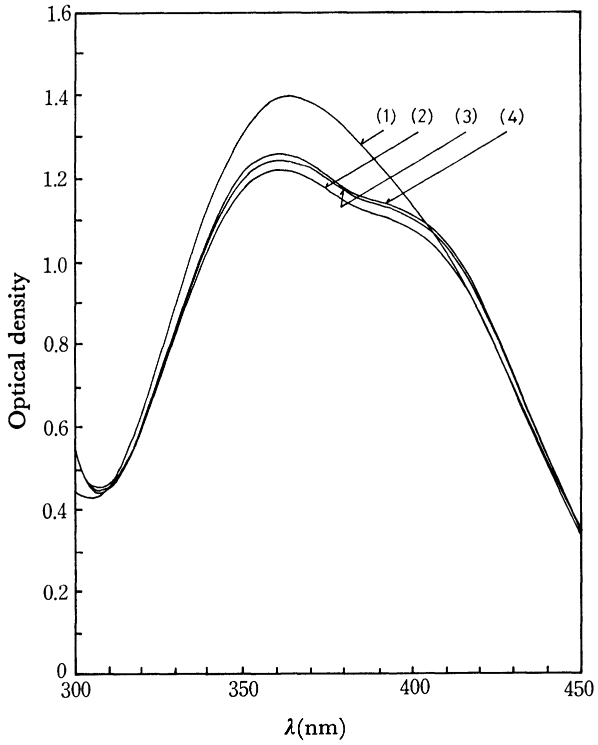

Fig. 4. Electronic absorption spectra of NQ in the presence of CTACl at various concentrations: none (1), 2.0×10^{-4} (2), 5.0×10^{-4} (3), $0.08-1.0\times10^{-2}$ M CTACl (4).

Association Complex of Quinonesulfonate and Cationic Surfactant. The NMR spectra indicate that the quinones with negatively charged group (SO_3^-) are associated with the positively charged nitrogen of the cationic surfactant. In fact, the association complex of PQ and CTABr gradually separated out of the freshly prepared equimolar solution of PQ and CTABr: mp 147—151 °C. IR (KBr disk) ν_{SO_2}, 1050, 1186; $\nu_{C=O}$, 1684; ν_{CH_2}, 2850, 2925; and δ_{CH_2}, 1465 cm^{-1}. The formation of the association complex was also verified by means of electronic absorption spectroscopy. The absorption spectra of NQ in the presence of various amounts of CTACl are shown in Fig. 4. When a small amount of CTACl is added to the aqueous NQ solution, the absorption band of NQ at 364 nm (ε_{max} 2.80×10^3) in water is split into two bands with λ_{max} at 361 (ε_{max} 2.50×10^3) and ~400 nm (ε_{max} ~2.0×10^3), respectively. The spectra of NQ in the presence of CTACl were in good agreement with those in organic solvents such as acetonitrile and alcohols. It is noteworthy that the absorption spectrum changes appreciably at the CTACl concentration far below the CMC. It may be suggested that the main body of NQ is in the hydrophobic environment which is provided by the long alkyl chain of the associated CTACl. The suggestion is supported by an examination of the absorption spectra of the equimolar solutions (5.0×10^{-4} M) of NQ and CTACl in water containing various amounts of acetonitrile. The π,π^* absorption band at 361 nm in water is shifted to 364 nm, and the one near 400 nm becomes obscure in 20—30% (v/v) acetonitrile–water solutions. The absorption spectrum observed in the 20—30% (v/v) acetonitrile–water agrees with that of NQ itself in water. At higher concentrations of acetonitrile (>40% (v/v)), the two absorption maxima at 361 and ~400 nm were restored. A possible explanation for the spectrophotometric behavior of the association complex in 20—30% (v/v) acetonitrile–water might be that the alkyl chain of the complex is elongated by the organic additive so that the water in the bulk phase become accessible to the main body of NQ.

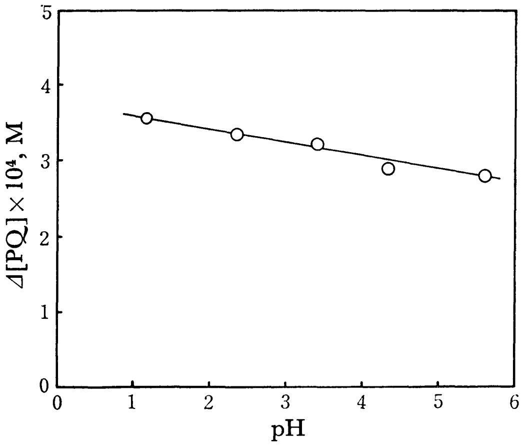

Fig. 5. Effect of pH on the disappearance of PQ in the presence of CTABr: $[PQ]_0=5.0\times10^{-4}$ M, $[SO_4^{2-}]=5.5\times10^{-2}$ M. The solutions were irradiated for 5 min at room temperature.

pH Effect. The pH effect on the photodecomposition of PQ in the presence of CTABr above the CMC is shown in Fig. 5. The pH (1.18—5.61) and the concentration of the sulfate ion ($[SO_4^{2-}]=0.055$ M) were adjusted with sulfuric acid and sodium sulfate, respectively. Disappearance of PQ is slightly depressed at higher pH. It appears that the photolysis of PQ is hardly affected by the hydroxide ions which are locally concentrated at the Stern layer of the cationic surfactant.

Deuterium Oxide Isotope Effect. The rate of formation of NQH_2 from NQ under irradiation in 99.8% D_2O is reduced in comparison with that in H_2O ($k_{H_2O}/k_{D_2O}=1.8$).[7] In the case of PQ (5.0×10^{-4} M), however, neither the disappearance of PQ nor the formation of

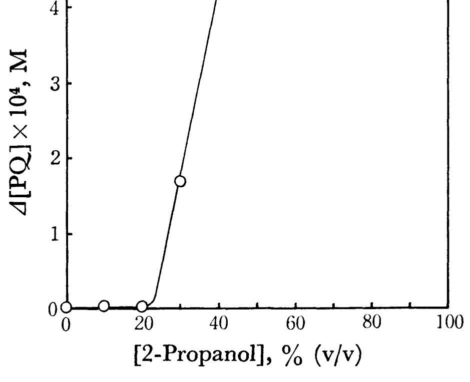

Fig. 6. Effect of 2-propanol concentration on the photoreduction of PQ in water. The solution of PQ (5.0×10^{-4} M) were irradiated for 2 min.

PQH_2 was affected by the use of deuterium oxide ($k_{H_2O}/k_{D_2O}=1.1$) in the presence of CTABr (4.0×10^{-3} M).

Photoreduction of PQ in 2-Propanol–water. In order to clarify the nature of the lowest photoexcited state of PQ in water, we examined the photochemical reduction of PQ in aqueous 2-propanol solutions. Figure 6 shows the effects of the concentration of 2-propanol on the photoreduction of PQ. Rapid photoreduction proceeds when the concentration of 2-propanol exceeds 20% (v/v), whereas PQ is scarcely photolyzed at low 2-propanol concentration. A linear relationship between the reciprocal of the quantum yields of the photoreduction and the reciprocal of the concentrations of 2-propanol is expected if the same chemical species is responsible for the reaction throughout the concentration range of 2-propanol investigated.[12] Contrary to expectation, a typical sigmoid profile was obtained (Fig. 6). The result suggests that the lowest excited state of PQ in water is an inactive π,π^* triplet, while that in 2-propanol is a n,π^* triplet. The critical concentration of 2-propanol for this disposition of the photoexcited species seems to be approximately 20% (v/v). The lowest photoexcited states of NQ are similarly suggested to be a π,π^* triplet in water and n,π^* triplet in organic media.[7]

Discussion

In the photoreduction of NQ in water to NQH_2,[7] it was found that:

1) The yield of NQH_2 is *ca.* 50%.

2) The quantum yield for the disappearance of NQ under irradiation at 365 nm is 0.118 ± 0.007 (pH5.00—6.80).

3) The radical anion of NQ ($NQ^{\cdot-}$) is detected by the ESR spectra when NQ is irradiated at pH 6.80, while no signal is observed at pH *ca.* 5.8.

4) The reactive species in this photoreduction is the π,π^* triplet of NQ.

5) The deuterium oxide isotope effect for the formation of NQH_2 (k_{H_2O}/k_{D_2O}) is 1.8.

Table 1. Effect of substrate concentration on quantum yields for the disappearance of NQ in water at 365 nm

$[NQ]\times 10^3$, M	Quantum Yield
1.97	0.122
3.99	0.076
5.98	0.064
8.00	0.049
10.00	0.045

We have found in the present work that the quantum yields for the disappearance of NQ decrease with increase of the initial concentrations of NQ (Table 1). Therefore the D/D* scheme postulated in the photoreaction of 9,10-anthraquinone-2-sulfonate[13,14] should be excluded from the possible mechanisms.

$$NQ^* + NQ \longrightarrow NQ^{\cdot-} + NQ^{\cdot+} \qquad (1)$$

We suggest the following sequence of reactions which lead to the photoreduction of NQ in water:[7]

$$NQ^* + OH^- \longrightarrow NQ^{\cdot-} + \cdot OH \qquad (2)$$

$$NQ^{\cdot-} + H^+ \longrightarrow NQH\cdot \qquad (3)$$

$$2NQH\cdot \longrightarrow NQH_2 + NQ \qquad (4)$$

$$NQ + \cdot OH \longrightarrow NQ(OH)\cdot \qquad (5)$$

The mechanism has not been confirmed, but it should be emphasized that water must be the reducing agent in the photoreduction of NQ.

The NMR spectra of the CTACl–micellar system containing NQ show that the SO_3^- group of NQ is associated with the positively charged nitrogen of CTACl so that the aromatic ring is incorporated into the hydrophobic micelle core. The electronic absorption spectra of NQ indicate that NQ is associated with CTACl so that the long alkyl chain surrounds the main body of NQ. Thus water can be excluded from the reaction site even at the concentrations of CTACl below the CMC. The photoreaction of NQ will be thus retarded in the presence of CTACl both above and below the CMC.

The photoreduction of PQ to PQH_2 was accelerated by the addition of the cationic surfactants (CTABr and CTACl). Neither ESR signal nor deuterium oxide isotope effect was observed in this case. Thus the mechanism of the photoreduction of PQ should differ from that of NQ in water. The surfactant concentration profile (Fig. 3) clearly indicates that the acceleration of the photolysis of PQ by cationic surfactants is not due to the ordinary micellar effects. As in the case of NQ–CTACl system, PQ and CTABr seem to form an association complex so that the main body of PQ would be surrounded by the long alkyl chain. The model might also be used to explain the fact that PQH_2 is completely stabilized toward oxidation with air in the presence of CTABr, whereas PQH_2 in pure water is rapidly oxidized to the original quinone. Under these circumstances, the photoexcited PQ would easily abstract hydrogen atom from the alkyl chain of the associated CTABr. If the hydrogen atom is abstracted from a free CTABr molecule, it is hardly expected for the reaction yield to reach an asymptotic value at such low CTABr concentration as in Fig. 3. The small deuterium oxide isotope effects is also explained by the same model. The photoreduction of PQ is influenced neither by the addition of sodium lauryl sulfate nor by polysorbate 80, inspite of the fact that they are expected to be better hydrogen donor than CTABr and CTACl due to the presence of $-OCH_2-$ group. All the data could be explained if the nature of the photoexcited state and its chemical reactivity vary with the change in environment surrounding PQ as summarised below.

1) The photoexcited PQ in water is considered to be the π,π^* triplet state. Since hydrogen abstraction is hardly induced by this particular species, no photoreduction takes place even in the presence of good hydrogen donors.

2) The lowest excited state of the association complex between PQ and CTABr is considered to be a n,π^* triplet so that hydrogen abstraction is easily induced in this case.

3) The hydrogen abstraction in the associated complex may be facilitated by the proximity effects of the alkyl chain (hydrogen donor) around the photoexcited PQ.

TABLE 2. THE EFFECTS OF SOLVENTS AND ORGANIC ADDITIVES ON THE PHOTOLYSIS OF ASSOCIATION COMPLEX BETWEEN PQ AND CTABr[a)]

Solvent	Additive	Irradiation time, min	$\Delta[PQ] \times 10^4$, M
H_2O[b)]	—	15	2.09
CH_3CN	—	20	0.84
CH_3CN	CTABr(5.0×10^{-3}M)	20	0.15
CH_3CN	2-propanol (1 vol%)	1.25	4.30

a) $[\text{Association complex}]_0 = 5.0 \times 10^{-4}$ M. b) $[PQ]_0 = 5.0 \times 10^{-4}$ M, $[\text{CTABr}] = 6.0 \times 10^{-4}$ M.

The effects of solvents and organic additives were examined in order to study the photochemical behavior of the association complex between PQ and CTABr (Table 2). The rate of reduction in acetonitrile was considerably less than that in water. The alkyl chain of CTABr surrounding the main body of associated PQ in water would be elongated in organic solvents. The rate of the hydrogen abstraction from the alkyl chain can be consequently reduced in acetonitrile. Addition of excessive CTABr quenches the photoreaction of the association complex in acetonitrile as expected from the heavy atom effects. It should be recalled, however, that the presence of CTABr in excess amounts did not quench the photolysis of PQ in water (Fig. 3). The difference in the effect of CTABr between these two solvents can be attributed to whether the reaction center of PQ is surrounded by the alkyl chain or not.

The same type of intramolecular hydrogen abstraction may also be expected to take place in the NQ-CTACl system as in the case of PQ-CTABr association complex. However, the photodecomposition of NQ in water was simply retarded on the addition of CTACl. It is suggested that the quantum efficiency for the hydrogen abstraction in the association complex between NQ and CTACl is much lower than that for the electron abstraction of NQ from the hydroxide ion.

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