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PHOTOCHEMICAL REACTION OF THE p-BENZOQUINONES IN MICELLAR SYSTEM[1)]

Koji KANO and Taku MATSUO
Department of Organic Synthesis, Faculty of Engineering, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

The photochemical reaction of p-benzoquinone and duroquinone in the presence of the surfactants has been investigated in aerobic phosphate buffer (pH 6.8). The photoreaction of p-benzoquinone was accelerated by the addition of sodium laurate (Φ/Φ_0 = 1.6) and sodium lauryl sulfate (Φ/Φ_0 = 1.4). Polysorbate 80 did not affect (Φ/Φ_0 = 1.0) and hexadecylethyldimethylammonium bromide markedly suppressed the photoreaction of p-benzoquinone (Φ/Φ_0 = 0.56). Meanwhile, the photoreaction of duroquinone was slightly suppressed by the anionic and non-ionic surfactants and was completely inhibited by the cationic one. The acceleration of the photoreaction of p-benzoquinone by the anionic surfactants was ascribed to the formation of the p-benzoquinone - micelle complex as confirmed by means of NMR spectroscopy. The results of the micellar effects on p-benzoquinone photochemistry suggest the formation of a cationic species as an intermediate.

Micelles formed by aggregation of surface active reagents in aqueous media have been utilized as enzyme models and/or to study the mechanisms of organic reactions.[2)] The amphipathic nature of these surfactants leads electrostatic stabilization or unstabilization of the transition state.[3)] The radical reactions are also affected by surfactants.[2)] For example, the photoreduction of riboflavin is considerably enhanced by the addition of polysorbate 80, sodium decyl sulfate, and polyvinylpyrrolidone.[4-6)]

The several studies on the photoreaction of p-benzoquinones in aqueous media have been published,[7-10)] the reaction mechanisms, however, have not been clarified. Then we used the micellar system to elucidate the photoreaction mechanisms of the p-benzoquinones in water. In this paper, we wish to report the preliminary results on the photoreaction of p-benzoquinone (p-BQ) and duroquinone (DQ) in the presence of the surfactants. Sodium laurate (NaL), sodium lauryl sulfate (NaLS), polysorbate 80 (P-80), and hexadecylethyldimethylammonium bromide (CEDAB) were used as the surfactants.

Photoproducts It has been reported that the photoproducts of p-BQ in anaerobic water are hydroquinone and benzene-1,2,4-triol.[8,9] The same products were obtained when an aerobic solution of p-BQ in phosphate buffer (pH 6.8) containing appropriate amounts of the surfactant was irradiated with a high-pressure mercury lamp. Namely, hydroquinone was a major product and 2-hydroxy-p-benzoquinone, which was produced by the rapid oxidation of benzene-1,2,4-triol in phosphate buffer, was a minor one.[11] In the photoreaction of DQ, only durohydroquinone was detected as the product by means of paper chromatography and UV spectroscopy

Micellar Effects on the p-Benzoquinone Photochemistry. Table 1 summarizes the quantum yields for the disappearance of p-BQ and DQ at 254 nm light in the aerobic phosphate buffer (pH 6.8). As Table 1 shows, the photoreaction of p-BQ was considerably accelerated by the addition of the anionic surfactants (NaL and NaLS) and was markedly suppressed by the cationic one (CEDAB). P-80 did not affect

Table 1. Quantum yield for the disappearance of p-BQ and DQ in micellar and non-micellar system at 254 nm[a]

Surfactant	p-BQ		DQ[b]	
	Φ	Φ/Φ_0[c]	Φ	Φ/Φ_0[c]
None	0.53 (0.66)[d]	1	0.018	1
NaL	0.86	1.63	0.017	0.95
NaLS	0.73	1.37	-	-
P-80	0.53	1.00	0.014	0.78
CEDAB	0.30	0.56	0.001	0.056

a) $[\text{p-BQ}]_0 = [\text{DQ}]_0 = 1 \times 10^{-3}$ M, $[\text{NaL}] = [\text{NaLS}] = 8 \times 10^{-3}$ M, $[\text{P-80}] = 0.029\text{-}0.32$ g/l, $[\text{CEDAB}] = 2 \times 10^{-3}$ M, in the 0.033 M of the phosphate buffer solution (pH 6.8), at room temperature

b) In the 10 vol% acetonitrile - phosphate buffer solution

c) Φ/Φ_0 is the relative quantum yield based on the non-micellar system.

d) The value in parenthesis is the quantum yield under nitrogen atmosphere.

the photoreaction of p-BQ. Meanwhile, the photoreaction of DQ was slightly suppressed in the presence of both NaL and P-80 and was completely quenched by CEDAB.

The quantum yields for the disappearance of p-BQ at 254 nm light in aerobic phosphate buffer (pH 6.8) are plotted as a function of NaL concentration in Fig. 1. The quantum yield becomes larger as the concentration of NaL is increased up to 0 01 M and becomes constant above this concentration These observations strongly suggest the presence of micellar catalysis in the p-BQ - NaL system Although the critical micelle concentration (CMC) of NaL is 0.024 M,(2) the CMC may be lowered in the phosphate buffer solution.

Investigation of p-Benzoquinone - Micelle Complex by Means of NMR Spectroscopy. The shape of ring proton signals of p-BQ changed with increasing the concentration of NaL at 80° (Fig 2) (12) The proton signal of p-BQ without NaL was observed

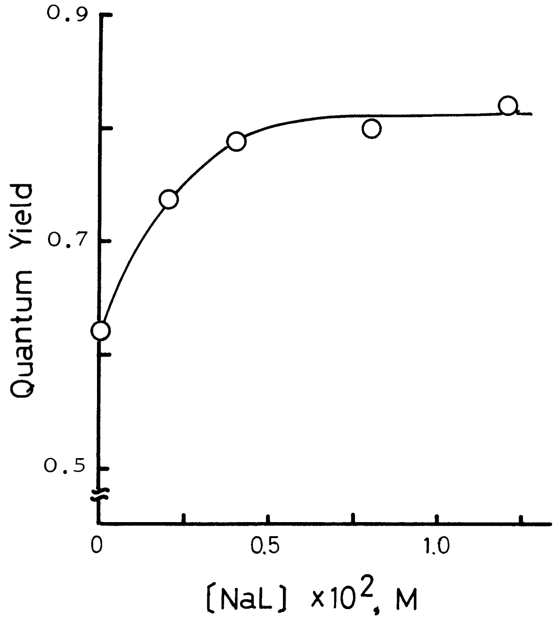

Fig. 1 Quantum yield for the disappearance of p-BQ (0.001 M) at 254 nm light plotted as a function of NaL concentration in the aerobic solution (pH 6.8).

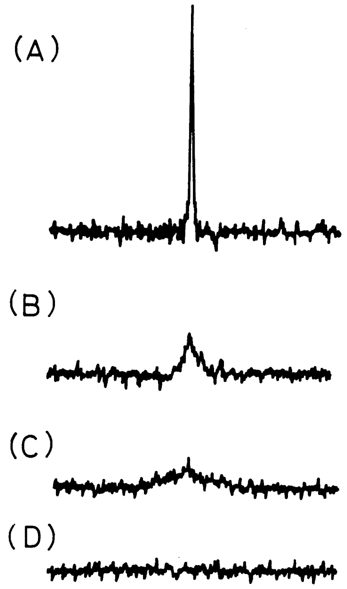

Fig 2. Observed NMR spectra of (A) 0.06 M p-BQ, (B) 0.06 M p-BQ and 2×10^{-4} M NaL, (C) 0 06 M p-BQ and 1×10^{-3} M NaL, and (D) 0.06 M p-BQ and 0.03 M NaL in 99.75 % D_2O at 80°. The proton signal of p-BQ is at -2 2 ppm from internal H_2O

at 2.2 ppm downfield from that of H_2O. This signal, however, was broadened out in the presence of a small amount of NaL and completely disappeared above CMC. The line broadening, observed here, may be caused by the strong interaction between p-BQ and NaL. Since a small amount of NaL caused the broadening of p-BQ signal, the interaction must be present even below CMC. Meanwhile, the NMR signal of p-BQ was slightly broadened out by P-80 and was not affected by CEDAB.

Salt Effects. The cationic surfactant, CEDAB, markedly inhibited the photoreaction of p-BQ and DQ. It has been known that the halogen ions inhibit the photoreaction of p-BQ and/or anthraquinone 2-sulfonate in water.[9,13] Moreover, the organic reactions in micellar system are sensitive to salt effects.[2,3] Then we studied the salt effects on the photoreaction of p-BQ and DQ with and without the surfactants. The photoreaction of DQ was inhibited in the same way by both CEDAB and Br^-. It is understood then that the inhibition of DQ photochemistry by CEDAB is due to Br^-. The inhibition of the photoreaction of p-BQ by the halogen ion (Br^-), however, was markedly reduced by the addition of NaL (Fig. 3). This protection effect of NaL may be interpreted as due to the electrostatic repulsion between the negative-charged head groups of micelles and the halogen ion.

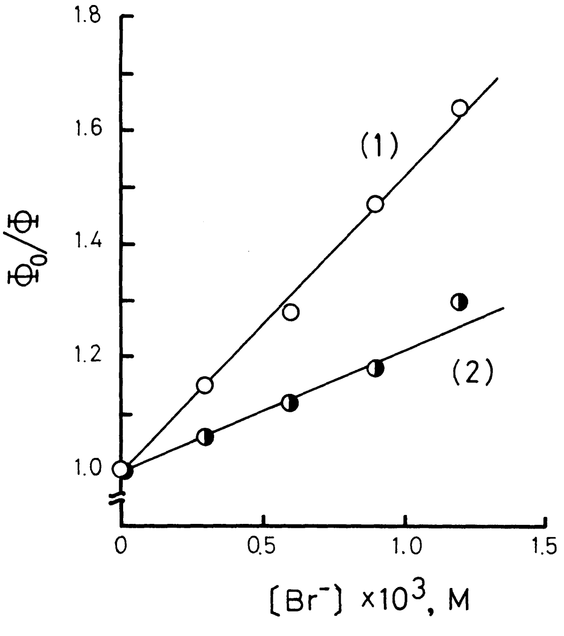

Fig. 3. Effect of Br^- on the photoreaction of p-BQ.

Φ_0 and Φ are the quantum yields in the presence and in the absence of KBr respectively. $[p\text{-BQ}]_0 = 1 \times 10^{-3}$ M, (1) in the absence of NaL, (2) in the presence of NaL ($[NaL] = 1.2 \times 10^{-2}$ M), in 0.033 M of phosphate buffer (pH 6.8), upon irradiation with a 100-W high-pressure mercury lamp by using a Riko rotary photolysis apparatus RH 400-10W at room temperature.

Discussion on the Reaction Mechanism. Both anionic and non-ionic surfactants accelerate the photoreaction of riboflavin in water,[4,5] which proceeds by the radical mechanism as confirmed by means of ESR spectroscopy.[6] In the photoreaction of p-BQ, however, only anionic surfactants enhanced the rate and the non-ionic one did not have any effect at all. In general, the ionic reaction which is accelerated by anionic surfactant is unaffected by non-ionic one and is inhibited by cationic one.[3] The results obtained here apparently suggest that the photoreaction of p-BQ in water proceeds by the ionic mechanism and that a cationic intermediate generated at some stage is stabilized by the binding with anionic micelles. On the investigation of wavelength dependence of p-BQ, the light corresponding to the $T_1 \leftarrow S_0$ (n,π*) transition, as well as $S_1 \leftarrow S_0$ (n,π*), is found to induce the reaction under discussion.[10] The energies of these excitations (E_S = 56, E_T = 50 kcal/mol)[14] are far below the dissociation energy of H-OH bond (117.8 kcal/mol) [15] Therefore, the present reaction can not be initiated by photolysis of the O-H bond of water which leads to the formation of ·OH and ·H radicals. In other words, the photoexcited p-BQ should follow an ionic reaction pathway The above micellar effects are certainly in accordance with this thermodynamic conclusion. The nature of the ionic species is not clear at the present stage of investigations. However, it might be possible that the polar reaction of photoexcited p-BQ will be somewhat analogous to those of 2,6-cycloheptadienone and the homologues in protic solvents.[16]

The above experimental observation indicates that the mechanism of the photoreaction of DQ in water differs from that of p-BQ. The detailed investigations on the reaction mechanisms and micellar catalyses for both p-BQ and DQ photochemistry are now in progress

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