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PHOTOCHEMISTRY OF SODIUM 1,2-NAPHTHOQUINONE-4-SULFONATE IN WATER[1)]

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It has been well-known that anthraquinones in the n,π* triplet state are strong sensitizers of photoinduced oxidation of alcohols.[2)] In this case, the corresponding anthrasemiquinone radicals are obtained as an intermediate.[3)] Recently, it was found that certain anthraquinones in photoexcited states abstract an electron from inorganic anions, alkoxide, and/or hydroxide ions to give the corresponding semiquinone radical anions.[4,5)] It should be noticed that not only the quinone in the n,π* triplet state (9,10-anthraquinone-2,6-disulfonate)[4)] but also the one in the C,T triplet state (2-piperidino-9,10-anthraquinone)[5)] abstracts an electron from the anions. Unlike the case of anthraquinones, few studies have been made on the photochemical oxidation-reductions of naphthoquinone derivatives in aqueous media. In this paper, we wish to report a one-electron transfer from hydroxide ion to photoexcited sodium 1,2-naphthoquinone-4-sulfonate (NQ).

When NQ (1.0×10^{-3} M) in aerobic water irradiated with a 100-W high-pressure mercury lamp, the intensities of the absorptions at 251.5 (log ε 4.30) and 365 nm (3.36) due to NQ decreased and new absorption bands with λ_{max} at 210, 234, 290, 300, and 338 nm appeared. The spectrum of the photoproduct was in good agreement with that of the authentic sample of sodium 1,2-dihydroxynaphthalene-4-sulfonate (NQH_2) (λ_{max} (log ε); 234(4.69), 290(3.75), 300(3.77), and 334 nm(3.64)) which was prepared by the sodium dithionite reduction of NQ. The formation of NQH_2 was further verified by its characteristic blue fluorescence with emission maximum at 470 nm. Since isosbestic points were observed at 206, 242, and 333 nm, it appeared that the photoreduction of NQ is quantitative. On the basis of the intensities of the absorption bands of the photolyzed solution when NQ completely disappeared, however, the yield of NQH_2 was estimated to be about 50%.

Since the pH values of the solution changed from 5.30 to 3.63 when 1.0×10^{-3} M NQ in pure water was irradiated, the quantum yield for the disappearance of NQ was determined by the use of the 0.033 M phosphate buffer solution (pH 6.80). The quantum yield obtained under the irradiation at 365 nm was 0.118±0.007 in the aerobic conditions. The quantum yields remained constant in the region between pH 5.00 and 6.80, and it was slightly reduced at pH 4.00 ($\Phi \sim 0.10$). At higher pH region (>pH 8.22), NQ reacted in the dark and unidentified products were obtained. Under the nitrogen atmosphere, the efficiency of the photoreaction of NQ was higher by a factor of *ca.* 2.2 than that in the air-saturated conditions. This indicates that the photoreaction of NQ in water proceeds *via* the triplet state.

In order to clarify the reaction intermediate, we examined the ESR spectra of the photolyzed solutions. Formation of a radical anion of NQ ($NQ^{\dot{-}}$) was detected when the air-saturated aqueous NQ solution (pH 6.80) was irradiated (Fig. 1). The number of lines and the *g*-value were 12 and 2.0049, respectively. In pure water (pH *ca.* 5.8), no ESR signal was obtained and NQ was rapidly photoreduced to NQH_2.

If $NQ^{\dot{-}}$ was formed by the one-electron transfer from the hydroxide ion to photoexcited NQ, the hydroxyl radical must be generated. However, the formation of hydrogen peroxide was not detected by the colorimetric test with titanium salt when the photolysis was carried out under the anaerobic conditions. The reactions between the hydroxyl radical and the quinones such as *p*-benzoquinone and anthraquinone sulfonates have been found to be diffusion-controlled processes:[6,7]

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

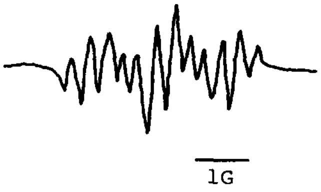

Fig. 1. ESR spectrum of $NQ^{\dot{-}}$.

$$Q + \cdot OH \xrightarrow{k} Q(OH)\cdot \qquad k \sim 10^{9} M^{-1} sec^{-1} \qquad (2)$$

Analogously, the same type of hydroxylation of NQ with hydroxyl radical may be suggested to take place. This suggestion is suported by the following facts:

1) The yield of NQH_2 was about 50%.

2) The quantum yield for the disappearance of NQ was reduced by a factor of *ca.* 2.5 on the addition of moderate amounts of hydroquinone (HQ), as a hydroxyl radical scavenger.

3) The reaction of NQ with Fenton's reagent gave a product without characteristic absorption bands in UV and visible regions.

On the basis of these data, we propose a reaction scheme of the photoreduction of NQ in water as follows:

$$NQ + h\nu \longrightarrow NQ^{*1} \quad (3)$$

$$NQ^{*1} \longrightarrow NQ^{*3} \quad (4)$$

$$NQ^{*3} + OH^{-} \longrightarrow NQ^{\cdot -} + \cdot OH \quad (5)$$

$$NQ^{\cdot -} + H^{+} \longrightarrow NQH\cdot \quad (6)$$

$$2NQH\cdot \longrightarrow NQH_2 + NQ \quad (7)$$

$$NQ + \cdot OH \longrightarrow NQ(OH)\cdot \quad (8)$$

where $NQH\cdot$ represents the semiquinone radical of NQ. The deuterium oxide isotope effects on the relative rate of NQH_2 formation at the initial stage (k_{H_2O}/k_{D_2O}) was 1.8, which may be taken to strongly indicate that the photoreaction of NQ in water involve the process of protonation (reaction (6)). On the basis of both the pH and isotope effects, it seems that the electron transfer to photoexcited NQ is fast and the protonation to $NQ^{\cdot -}$ is relatively slow.

The n,π* absorption band of NQ in 90% (v/v) aqueous acetonitrile was observed at 520 nm (ε ∿ 60). This band, however, was hidden under the strong π,π* absorption band in pure water. Then we studied the effects of water concentration on the NQ photochemistry. In acetonitrile-water system, the reactivity of photoexcited NQ markedly increased when the concentration of water exceeded 70% (v/v), as shown in Fig. 2. The similar results were obtained when the aqueous NQ solutions containing various amounts of 2-propanol were irradiated (Fig. 3). The typical sigmoid profile indicates that the photoexcited NQ selectively reacted with water at lower 2-propanol concentrations (<40% (v/v)) and with 2-

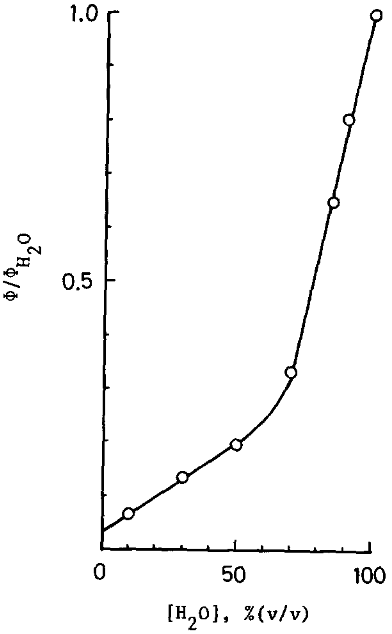

Fig. 1. Effects of water concentration on NQ photoreaction. Acetonitrile was used as a diluent.

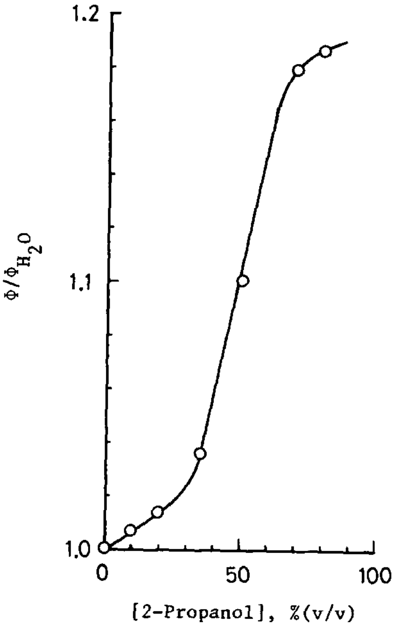

Fig. 2. Effects of 2-propanol concentration on NQ photoreaction in water.

propanol at higher 2-propanol concentrations (>60% (v/v)). The reaction of photoexcited NQ with water may compete with that of 2-propanol only at the intermediate concentrations of 2-propanol. These findings suggest that the electronic structure of NQ in the lowest triplet state varies with the polarity of the solvents. We believe that the lowest triplet level of NQ in water is π,π^* in character, rather than n,π^*.

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