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Photolysis of *p*-Benzoquinone in Aqueous Solution. Possibility of a Polar Mechanism in the Primary Process

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Synopsis. The photochemistry of *p*-benzoquinone in water was investigated spectrophotometrically. The effect of *p*-nitroso-*N,N*-dimethylaniline as an additive confirmed a non-radical mechanism. The small positive deuterium isotopic effect suggests an electrophilic attack of the excited *p*-benzoquinone on water.

The photochemical reactions of *p*-benzoquinone (BQ) have been extensively studied in alcoholic solutions but less in aqueous solutions. In the photolysis of aqueous solutions of BQ, hydroquinone (HQ) has been isolated as the sole stable product in addition to the transient formation of benzene-1,2,4-triol (BTO) and 2-hydroxy-1,4-benzoquinone (HOBQ).[1] From the results it was suggested that the photolysis of BQ in aqueous solutions consists of a two stage process; formation of BTO from the reaction of the excited BQ with water molecule in the primary process, and dark reaction of BTO with BQ to yield HQ and HOBQ which is unstable in water in the secondary process. Kurien and Robins[2a] and Joschek and Miller[2b] proposed a radical mechanism for the primary process: the excited BQ abstracts a hydrogen atom from a water molecule forming semiquinone and a hydroxyl radical, the hydroxyl radical reacting with either the semiquinone radical or another BQ, ultimately resulting in the formation of BTO. Kano and Matsuo[3] suggested the possibility of an ionic mechanism including a cationic intermediate from the effect of micellar system on the photolysis of BQ in aqueous solutions. This paper presents some evidences supporting a polar mechanism in the primary process.

p-Nitroso-*N,N*-dimethylaniline(NDA), an effective hydroxyl radical scavenger,[4] was dissolved in an aqueous solution of BQ and an aqueous solution of sodium 9,10-anthraquinone-2-sulfonate(AQS), respectively. Absorption peaks of BQ and AQS were not affected by the added NDA. No direct photolysis of NDA occurred under our experimental conditions. Variation in absorbance during the course of irradiation with 313 nm light was followed at 247 nm, 255 nm, and 440 nm for BQ, AQS, and NDA, respectively. The results are shown in Fig. 1. No detectable change in the absorbance of NDA was observed in the photolysis of BQ in the BQ–NDA mixed system, while an appreciable decrease was observed in that of AQS in the AQS–NDA mixed system. The former result indicates that the photolysis of BQ takes place *via* a non-radical process. The latter result reflects a radical intermediate formation in the photolysis of aqueous AQS.[5]

The only basis for the radical mechanism[2a] was the halogen ion effect. Decrease in the quantum yield by the addition of halogen ion was ascribed to its function as radical scavenger. However, the effect of halogen ion should result from the quenching function as well as in the photolysis of aqueous AQS.[6] The Stern-Volmer plot for Cl^- as quencher gave a straight line.

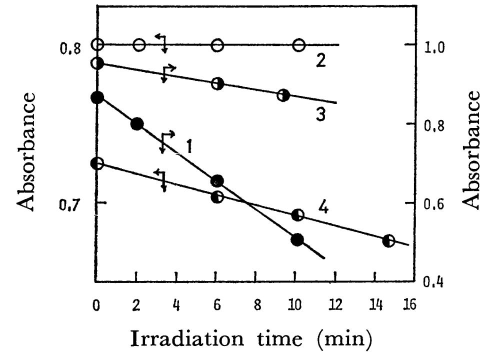


Fig. 1. Variations in the absorbance of BQ, AQS, and NDA with irradiation time.
a) BQ–NDA mixed system. [BQ] = 3.80×10^{-5} M, [NDA] = 2.34×10^{-5} M. Change in the absorbance; 1) at 247 nm for BQ, 2) at 440 nm for NDA.
b) AQS–NDA mixed system. [AQS] = 1.80×10^{-5} M, [NDA] = 2.12×10^{-5} M. Change in the absorbance; 3) at 255 nm for AQS, 4) at 440 nm for NDA.

The photochemistry of pyrimidine base in water has been investigated widely because of its significance in photobiology.[7] The photohydration of pyrimidine was suggested to occur *via* an electrophilic attack of the excited base on water. The small positive value ($k_H/k_D = 1.18$) of the deuterium isotopic effect for uracil in acetonitrile–D_2O was ascribed to a secondary isotopic effect and provided strong evidence for the confirmation of an electrophilic attack mechanism.[8] The rate of photolysis of BQ in water (Fig. 2) was somewhat lower in D_2O than in H_2O. This small isotopic effect ($k_H/k_D = 1.15$) suggests that the rate-determining step of the photolysis of BQ in water is

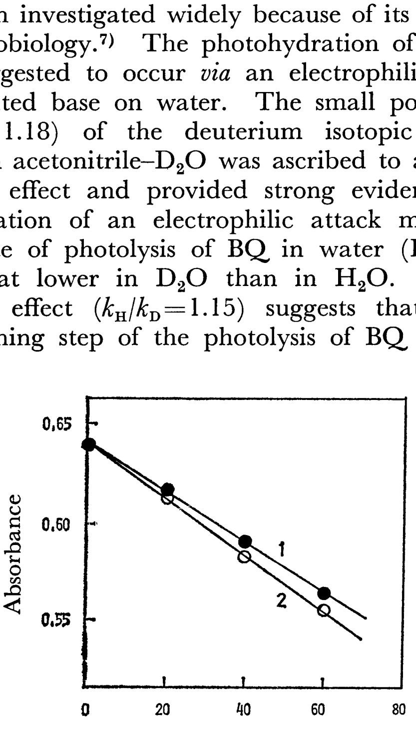
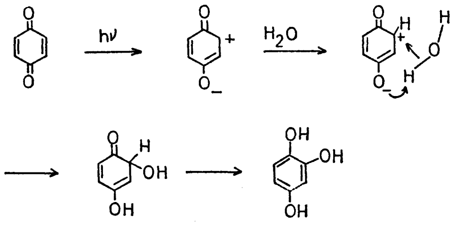


Fig. 2. Photolysis of BQ in H_2O and in D_2O.
1) in D_2O, 2) in H_2O. [BQ] = 3.0×10^{-5} M.

not a direct hydrogen abstraction from water but an electrophilic attack of the excited BQ on water, as well as uracil. There are several reports on the photo-induced polar reactions of cyclic enones[9] and dienones.[10] These polar reactions are explicable in terms of the contribution of polar state in the product controlling step.[11] The primary process of the photochemical reaction of BQ in water seems to pass through a polar intermediate as shown in Scheme 1.



Scheme 1.

Experimental

A Toshiba SHL-100 UV high-pressure mercury lamp was used as a light source. A combination filter, a Toshiba UV-D 25 filter, an aqueous nickel sulfate solution and a Pyrex filter were employed to obtain the light of 313 nm. The light intensity determined with aqueous potassium ferrioxalate as an actinometer was 7.1×10^{18} quanta$\cdot$l$^{-1}\cdot$min.$^{-1}$ The photolysis in the presence of NDA was carried out with a light of wave length below 350 nm. The samples were irradiated in spectrophotometer cells at room temperature. The rate of photolysis for BQ was followed by the change in absorbance at 247 nm. HQ was isolated as the sole stable product but separation of HOBQ which is unstable in the dark was unsuccessful. The formation of BTO was confirmed by UV spectrum ($\lambda_{\max}$ 289 nm, $\varepsilon=3300$). Spectra were measured on a Shimadzu UV-200 recording spectrophotometer. BQ was sublimed (mp 116°). NDA was recrystallized from ligroin (mp 86—87°). Water was purified by the usual method.

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