The Photochemical Reaction of *p*-Benzoquinone in Water

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(Received October 27, 1971)

Although the photochemical oxidation of alcohols by quinones has been extensively studied, few investigations of the photolysis of quinones in aqueous solutions have been done until recently. Broadbent[1] has reported that photoexcited 9,10-anthraquinonesulfonates decompose water to generate the ·OH radical. Hughes and Uaboonkul[2] have reported that photoexcited 9,10-phenanthrenequinone abstracts a hydrogen atom from water to generate a semiquinone radical, which then reacts with triphenylphosphine to produce a dipolar form of 2,2,2-triphenyl-1,3,2-dioxaphospholene. In this communication, we wish to report some preliminary results on the photochemistry of *p*-benzoquinone in water.

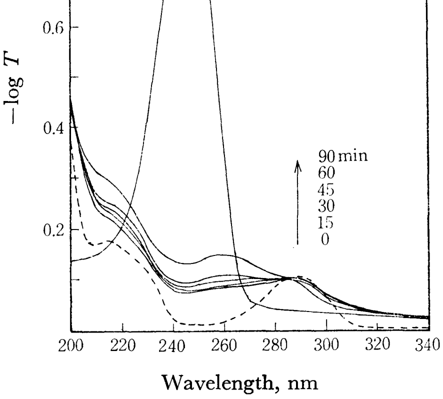

Fig. 1. The UV-spectral change of the photoreaction of *p*-benzoquinone in water. For UV-spectra measurement, 0.8 m*l* of the photolyzed solution was exactly diluted to 20 m*l* with water. The dotted line is the spectrum of the authentic sample of hydroquinone (4×10^{-5}M).

Figure 1 shows the UV-spectral change during the course of the photolysis of a 1×10^{-3}M solution of *p*-benzoquinone in water on irradiation with an immersion-type 130-W high-pressure mercury lamp in a stream of nitrogen. Upon irradiation, the reaction solution became dark orange; this seemed to be due to the formation of quinhydrone. The absorption spectrum of the final photoproduct was the same as that of hydroquinone. Paper chromatography also suggested the formation of hydroquinone (a Toyo filter paper No. 50 was used. Solvent: absolute ethanol; color-producing reagents: ferric chloride and potassium ferricyanide; R_f value of hydroquinone: 0.87).

A solution of *p*-benzoquinone (32.4 mg, 3×10^{-3} mol) in water (300 m*l*) was irradiated with an immersion-type 130-W high-pressure mercury lamp for 30 min at room temperature in a stream of nitrogen. The photolyzed solution was then extracted with ether. The residue obtained upon the removal of the ether was purified by alumina-column chromatography with absolute ethanol and then recrystallized from benzene. Colorless needles of hydroquinone were thus obtained; mp 172—173°C; 12.3 mg (37.2%). In this reaction, we could not detect hydrogen peroxide, which might be produced by the coupling of ·OH radicals.

In the UV spectrum of *p*-benzoquinone in water, the n,π^* and π,π^* absorption maxima were observed at 425 nm ($\varepsilon_{max}=20$) and 246 nm ($\varepsilon_{max}=2.2\times10^4$) respectively. Meanwhile, Kuboyama[3] has reported that the absorption band of *p*-benzoquinone at 539 nm ($\varepsilon_{max}=0.2$) in *n*-heptane can be attributed to the $T_1\leftarrow S_0$ transition (n,π^*). Therefore, we examined the wavelength dependence of the *p*-benzoquinone photochemistry in water. Anaerobic aqueous solutions of *p*-benzoquinone were irradiated with 313 nm (a combination filter of a Toshiba UV-D25 filter, an aqueous nickel sulfate solution, and carbon tetrachloride), 436 nm (a combination filter of a Toshiba V-Y42 filter and a Toshiba V-V42 filter), and >550 nm (a Toshiba V-O56 filter) light respectively. In all cases, *p*-benzoquinone was photolyzed to produce hydroquinone. Since the shoulder of the n,π^* band of *p*-benzoquinone is not observed at wavelengths beyond 550 nm, the n,π^* triplet of *p*-benzoquinone generated by the $T_1\leftarrow S_0$ transition must participate in this photoreaction.

Table 1. Quantum yields for the disappearance of *p*-benzoquinone in water at 313 nm

p-Benzoquinone, $\text{M}\times10^3$	Quantum yield
9.85	5.2
4.78	6.0
1.00	5.1
0.45	5.8

We determined the quantum yields for the disappearance of *p*-benzoquinone in the anaerobic aqueous solutions at 313 nm. The results are shown in Table 1. The quantum yields were independent of the initial concentrations of *p*-benzoquinone. This finding suggests that a bimolecular deactivation of photoexcited *p*-benzoquinone does not occur, and that photoexcited *p*-benzoquinone does not abstract a hydrogen atom from the quinone ring. Therefore, it seems that water is the hydrogen donor in this reaction. By the way, the quantum yields were greater than unity in all cases. This indicates a chain reaction. The mechanisms of the chain reaction are now under investigation.

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[1] A. D. Broadbent, *Chem. Commun.*, **1967**, 382.

[2] A. N. Hughes and S. Uaboonkul, *Chem. Ind.* (London), **1967**, 1253.

[3] A. Kuboyama, *Report of the Government Chemical Industrial Research Institute* (Tokyo), **59**, 347 (1964).